

Collection and Interpretation of
Level 1 IR and LRMS Data

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COLLECTION AND INTERPRETATION OF LEVEL 1 IR AND LRMS DATA

by

Alvia Gaskill, Jr.
William F. Gutknecht
Systems & Measurements Division
Research Triangle Institute
Research Triangle Park, North Carolina 27709

Prepared for

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Abstract

Collection and Interpretation of Level 1 IR and LRMS Data

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Alvia Gaskill, Jr.
William F. Gutknecht

Contract No. 68-02-2688
Task Directive 101

Approaches to measurement and interpretation of infrared (IR) and low resolution mass spectra (LRMS) taken by four Environmental Protection Agency (EPA) contractors following the guidelines of the Level 1 Environmental Assessment Program were evaluated. The mechanism of evaluation involved supplying each contractor with test spectra and samples for analysis and interpretation. Using IR, the contractors identified 55 to 85 percent of the structural moieties present in the various samples or indicated by the various test spectra, with 85 percent being approximately the maximum attainable. Sources of error in IR measurement included analyst-to-analyst variation in signal location of $\pm 5\text{-}10\text{ cm}^{-1}$ and failure to optimize signal intensity through proper loading of the salt plates or KBr pellets. IR interpretation errors disclosed were errors of omission and assignment. To improve IR data quality, all significant signals must be interpreted, including those complementary signals that support or refute other assignments; also, reasonable, alternative interpretations must be considered. The contractors identified 50 to 90 percent of the compound classes represented using LRMS. LRMS interpretation errors disclosed were failure to find molecular ions, reporting molecular ions as fragment ions and vice versa, incorrectly identifying molecular ions and incorrectly assigning ions to homologous series. To improve LRMS data quality, the reference series Eight Peak Index of Mass Spectra should be used, intensity and mass/charge range criteria set to simplify spectra, the LC fraction data used with caution, and IR and LRMS data analyzed independently to avoid bias.

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SECTION 1

INTRODUCTION

1.1 OBJECTIVE OF THE STUDY

Infrared (IR) spectrometry and low resolution mass spectrometry (LRMS) are two of the principal methods used in the Level 1 program for semiquantitative determination of organic classes and compounds. These methods have proven suitable for this task in a variety of successful Level 1 studies. It appears, however, from several evaluations of the Level 1 program, that these techniques are not always being used by environmental assessment contractors to maximize the output of useful data from Level 1 LC fractions 4, 5, and 6. This problem could arise from a number of sources; for example, poor sample preparation, poor instrumental techniques, or weakness in spectral interpretation. One objective of the study described herein has been to identify these sources of difficulty and to suggest ways to overcome or reduce their magnitude. A second objective has been to identify the positive components of the contractors' use of these techniques that lead to high quality results.

1.2 APPROACHES TO INVESTIGATION

There have been two stages in this study. In the first stage, six IR and six LRMS test spectra were prepared using samples that varied in both complexity and variety of organic functional group content. The spectra were acquired using six samples blended to represent Level 1 LC fractions 4, 5, and 6. There were two different samples for each of the three LC fractions and the spectra were prepared following Level 1 procedures. These spectra were sent to four contractors selected by the EPA Project Officer (Arthur D. Little, Inc., Battelle Columbus Laboratories, Southern Research Institute, and TRW Systems).

The contractors were requested to interpret the spectra as normal Level 1 spectra. A copy of the organic analysis chapter of the Level 1 Environmental Assessment Manual (Second Edition, Lentzen et al.) was provided for guidance in this task. No special efforts were to be made with these spectra beyond

that expected for Level 1 work. However, the contractors were asked to clearly indicate the spectral characteristics leading to the identification of functional groups, structural characteristics, or, when possible, individual compounds or compound classes. Using the analysis sheets provided, the contractors were to spell out clearly the reasoning behind each assignment, including information about peak wavelength or mass, peak magnitude or shape, patterns of peaks, or correlation with LC fraction number. Also, if the LRMS data proved useful to the IR interpretation and/or vice versa, the contractor was to state this fact, and explain.

The returned test results were studied with respect to accuracy, thoroughness of interpretation, approach to interpretation, etc. On the basis of these results, two synthetic samples were prepared and sent to the contractors for both IR and LRMS analysis. The samples for this second stage of the investigation were prepared to represent LC fractions 5 and 6. They were prepared principally from compounds that were used to prepare the stage one spectra and that had proved difficult to identify previously. This was done, in part, to determine if measurement of their own spectra would improve the contractors' abilities to make accurate analyses as well as to test the residual problems identified with the stage one spectra. Included with the two synthetic samples was a sample of tar from a coal gasification unit. This sample was to be separated using the Level 1 LC scheme, and fractions 4, 5, and 6 were to be analyzed using IR and LRMS. The spectra and interpretation results from this second stage of the study were returned and have been studied in conjunction with the earlier interpretation results with regard to accuracy and sources of error. Approaches to spectral interpretation have also been investigated through personal visits and/or telephone conversations with the contractor spectroscopists. The results of these investigations and studies are presented in detail in Sections 5 through 7. Recommendations for improvement of the IR/LRMS techniques, as used in Level 1 environmental assessment, are presented in the next section. These recommendations are based on the observed sources of difficulty and on the activities of the spectroscopists that contributed to high quality data.

SECTION 2

SUMMARY AND CONCLUSIONS

The IR and LRMS results have been studied with regard to accuracy and sources of error. Approaches to spectral interpretation have also been investigated through personal visits and/or telephone conversations with the contractor spectroscopists. The results of these investigations and studies are presented in greater detail in Sections 5 through 7. They are summarized here, and recommendations for improvement of the IR/LRMS techniques as used in Level 1 environmental assessment are presented.

2.1 IR STUDIES

2.1.1 IR Measurements

In addition to interpreting the six spectra provided, the contractors made IR measurements with three samples blended to represent Level 1 LC fractions 5 and 6--two synthetic mixtures and a sample of coal tar. Three components of the measurement process were observed to have a significant effect upon the final interpretation results. Least significant was the variation from contractor to contractor in band location for signals from the same structural source. A second component was failure to optimize band intensity, which generally resulted from use of either insufficient or excess sample quantity. The third factor was the weakness or absence of bands in the 4000 to 2000 cm^{-1} range in spectra obtained with KBr pellets as compared to those obtained with salt plates. This may be due to interaction with the KBr pellet, cloudiness, or loss of volatile compounds during pellet preparation.

2.1.2 IR Interpretation

The results of the contractors' interpretation efforts were generally acceptable. Accuracy of identification of functional groups and/or structures present in the sample and also indicated by the spectra ranged from 60 to 80 percent.

Several types of errors contributed to these levels of identification. A number of errors are apparently the result of simple incorrect assignments. A greater number of errors are the result of making rational though incorrect interpretations, which result from the simple fact that there are different structures that give rise to bands at very nearly the same wave-number. The greatest number of errors appear to result from incomplete use of available data. In many instances, bands indicating the presence of certain structures simply were not interpreted. In other cases, bands that would support or refute assignments based on other bands were either not interpreted or were interpreted as being due to some other structure.

2.1.3 IR--Recommendations

Some of the errors observed arise from problems in measurement. Most arise, however, from problems in interpretation. Interpretation errors are apparently due to unintentional oversights, incorrect information about the location of bands due to certain structures, experience-related bias in favor of certain structures of compounds, failure to use bands in the spectra that would support or refute the interpretation of the band in question, and/or failure to consider all reasonable interpretations of the bands in a spectrum. Such errors are best eliminated by having the spectroscopist occasionally verify his or her interpretations by using reference materials and/or having interpretation results occasionally checked or audited by a second, outside spectroscopist or by providing Level 1 EPA contractor spectroscopists with standardized IR band assignment charts/tables and an instructional course on interpretation of IR spectra.

It has been observed that the quality of the results presented by each spectroscopist is, in general, a reflection of his or her level of experience and the time given to interpretation, though the correlation is not strong. In fact, it is the thoroughness of the interpretation that seems to have the greatest bearing on the quality of the results. A thorough interpretation requires, however, that the spectroscopist consider all possible (and reasonable) functional groups and structures that could be present in a sample.

2.2 LRMS STUDIES

2.2.1 LRMS Measurements

The contractors obtained low resolution mass spectra on three samples--two synthetic mixtures blended to represent Level 1 LC fractions 5 and 6,

and a sample of coal tar. All samples were analyzed using a direct insertion heated probe with a series of spectra taken on a sample as the sample was being volatilized from the probe. Three out of four analysts obtained their spectra via digital readout data recording systems. One analyst obtained the spectra via an analog oscillographic trace.

No differences in the quality of the spectral data obtained or in the results of the contractors' analyses of these data were found to be attributable to the instrumentation or measurement techniques used. For example, although one contractor found that spectra taken at low (15 eV) ionizing voltage was useful in the identification of molecular ions not easily disclosed from the 70-eV spectra, the other contractors did not use this approach, nor did it appear to significantly affect the overall quality of results for these three samples.

2.2.2 LRMS Interpretation

The results of both stages of the spectral interpretation test indicated that 50 to 90 percent of the compound classes or categories present in the eight synthetic mixtures were correctly identified. The categories most often missed were fused ring acids, ketones, and phenols. Single ring phenols known to be present in the tar sample were correctly identified by three out of four contractors.

Five types of LRMS interpretation errors observed in the results from the spectral interpretation test are:

1. Errors of omission--not noting the presence of molecular ions.
2. Reporting molecular ions as fragment ions.
3. Reporting fragment ions as molecular ions.
4. Incorrectly identifying molecular ions.
5. Incorrectly assigning ions to a homologous series.

Failure to find molecular ions accounted for almost half the categories and compounds missed in the test spectra and mixtures.

Factors other than errors in assignment and errors of omission that affect analysis accuracy include the approach to interpretation taken and the degree of interaction with the IR analyst to produce a composite report on the sample. The analyst's experience (years spent as a mass spectro-

scopist) and the time given to interpretation had little bearing on these results. A composite list of the major factors that correlate either positively or negatively with the more successful spectral interpretations include as positive correlates the search for molecular ions, the search for the eight most abundant fragment ions, the setting of intensity and mass/charge range criteria for peaks to be studied in a spectrum, the use of the tabulated reference source, the Eight Peak Index of Mass Spectra (Imperial Chemical Industries), and the careful consideration of the IR data analyses in making final compound class/compound assignments. After reviewing the IR interpretation results, the LRMS analysts in many cases revised their observations by adding new categories and/or compounds and by confirming or rejecting the presence of compounds already listed based on the LRMS alone.

2.2.3 LRMS Recommendations

Five recommendations regarding LRMS measurement and spectral interpretation have been developed. These are:

1. Low (15 eV) ionizing voltage spectra can be used to aid in the identification of molecular ions although this is not essential. It is especially useful if the 70-eV spectrum does not permit relatively straightforward interpretation.
2. Analysts who do not have the instrumental capability to switch from 70 eV to 15 eV during a run should be allowed to use chemical ionization (CI) mass spectrometry if and only if it can be established that CI provides significantly more information on molecular ions than 70-eV EI spectra.
3. The Eight Peak Index of Mass Spectra should be used to interpret and verify spectra. Other reference sources such as the EPA/NIH Data Base (Heller and Milne), The Mass Spectral Correlation Tables, and the American Petroleum Institute Index are useful for certain cases but, as general references, they tend to be less complete or inaccurate.
4. Peak intensity and m/e range criteria should be set above which all ions will be as fully accounted for as possible. These criteria may vary from sample to sample and spectrum to spectrum.
5. A series of spectra should be obtained as a sample is being volatilized from the probe. The spectra should be examined individually as well as in relation to each other.

In addition, several recommendations have been developed that apply to both IR and LRMS techniques. These are:

1. The LC fraction table in the Level 1 Manual or any other such similarly constructed table should not be used to exclude the presence of any category. Such a table should only be used as a very rough guide to verify the presence of a category or compound already indicated on the basis of more reliable factors such as IR and LRMS data.
2. The IR and LRMS analysts should first analyze their data independently to avoid bias and then consult with one another to produce a composite report. Irreconcilable differences should be noted and both categories identified should be reported if the differences cannot be resolved.
3. Analysts should adhere rigidly to the nomenclature for categories given in Table 17 in the Level 1 Manual. Nomenclature for compound identification must be uniform and not based on personal preferences. The International Union of Pure and Applied Chemists nomenclature for compounds should be used by all contractors.
4. All LRMS and IR data should be reported on the Level 1 forms exactly as specified.
5. Contractors should familiarize themselves with the sample source they are studying and the chemistry, if any, taking place. Under no circumstances should the analysts limit themselves to a "list of compounds" they feel will probably be present.
6. In general, the LRMS and IR data should be used as primary data inputs to sample interpretation. Other inputs, such as LC fraction, sample source, and previously generated data on similar sources, should be given less weight.
7. Polyfunctional compounds like 9-fluorenone-4-carboxylic acid should be listed as both possible categories (in this case, acid and ketone). Quantitation in such cases should be investigated.
8. All contractors performing Level 1 LRMS and IR analyses should be given the opportunity to complete spectral interpretation tests on appropriate real and synthetic test samples that will measure the contractor's analytical and interpretive abilities. In order to relate the test results to actual sample analyses, these tests must have cost/time considerations. For example, the contractor should spend "X" hours and should prepare the sample(s) "Y" number of times. Some idea must be given of the intensity of the application of the technique.
9. In conjunction with 8, all contractors performing Level 1 LRMS and IR analyses should receive guidelines documents illustrating efficient and accurate ways in which Level 1 LRMS and IR can be performed. These guidelines should contain numerous completely worked out example spectra. Also, along with these training sets, workshops should be held during which Level 1 LRMS and IR experts will interact and exchange ideas.

Implementation of 1 through 9 will improve the quality of the data generated by contractors now performing Level 1 LRMS and IR as well as aid those laboratories just beginning Level 1 work.

SECTION 3
EXECUTIVE SUMMARY

3.1 IR STUDIES

The results of the contractors' measurement and interpretation efforts were generally acceptable. Accuracy of identification of functional groups and other structural moieties indicated by the synthetic spectra, the spectra from the synthetic samples, and spectra from the tar samples are shown in Table 1.

An accuracy level of 80 percent is considered very acceptable; in general, identification at this accuracy level means that only the structures most difficult to identify have been missed. Contractors A and C achieved less than 80 percent accuracy levels on two sample types principally because of low-quality spectral data. Contractors B and D achieved low levels principally because of inaccurate and incomplete spectral interpretations.

3.1.1 IR Measurements

In addition to interpreting the six spectra provided, the contractors made IR measurements with three samples--two synthetic mixtures and a sample of coal tar. Three components of the measurement process were observed to have a significant effect upon the final interpretation results. These are:

TABLE 1. ACCURACY OF FUNCTIONAL GROUP/STRUCTURE
IDENTIFICATION USING IR (%)

	Contractor			
	A	B	C	D
Test spectra	85	65	85	60
Test samples	55	55	80	80
Tar samples	80	70	65	85

- Variation in band location from contractor to contractor for bands from the same structural source.
- Signal intensity not optimized.
- Weakness or absence of bands in the 4000 to 2000 cm^{-1} range in spectra obtained with KBr pellets.

The variation in band location was in the range of ± 5 to $\pm 10 \text{ cm}^{-1}$. This variation was due both to variation in the actual locations of the bands in the spectra and also inexact assignment of the band locations by the analyst.

Signal intensity cannot always be optimized because of insufficient sample quantity; however, overloading of the salt plate or KBr pellet, which can and must be controlled, was observed and had the effect of weak or medium signals being falsely identified as medium or strong signals.

The most serious of the three factors observed was the weakness or absence of signals in the 4000 to 2000 cm^{-1} range in spectra obtained with KBr pellets as compared to those obtained with salt plates. This weakness or absence may be a result of interaction with the KBr, energy loss due to cloudy pellets, or a loss of volatile compounds which occurs during preparation of the KBr pellets. For example, the two contractors using KBr pellets missed aliphatic CH in the 3000 to 2900 cm^{-1} range apparently because of insufficient signal; the two using salt plates did have signals attributable to aliphatic CH in this range.

3.1.2 IR Interpretation

Several types of errors were observed to affect the levels of accuracy of identification achieved. These include failure to interpret bands, simple assignment errors, assignments made that were rational but not correct, and failure to use alternate bands to support or dispute assignments based on other bands.

3.1.2.1 Bands Not Used--

Both primary and secondary bands for structural or functional groups were not used. Examples of data not used are presented in Table 2.

3.1.2.2 Errors in Assignment--

Examples of errors in assignment, which were not often made, are shown in Table 3.

TABLE 2. SELECTED EXAMPLES OF UNASSIGNED BANDS
FOUND IN VARIOUS SPECTRA

<u>Band not assigned, cm^{-1}</u>	<u>RTI assignment</u>
2930, 2850	Saturated CH
1680, 1670	Carbonyl
1430, 1240	Coupling of acid OH/C-O groups
1450, 1465, 1390, 1380, 1364	CH_3
1240, 1160, 1100	C-O of alcohol

TABLE 3. SELECTED EXAMPLES OF ERRORS IN ASSIGNMENT OF BANDS

<u>Band, cm^{-1}</u>	<u>Apparently erroneous assignment</u>	<u>Apparently correct assignment</u>
1805	Carbonyl	Overtone or summation band
1600	Unsaturated CH	Aromatic C=C
1480, 1470	Unsaturated CH	CH_3
1510	C-N	Aromatic C=C
3052	OH	Unsaturated CH

3.1.2.3 Rational, Though Incorrect, Assignments--

Rational, though incorrect, assignments arise because different structures and functional groups give rise to bands in the same wavelength regions. Examples of these errors are given in Table 4.

3.1.2.4 Incomplete Use of Available Information--

Most structures give rise to several bands that have regular relationships in terms of wavelength, magnitude, and breadth. Such complementary bands serve both to support and dispute assignments. Examples of such complementary data not used are:

1. A band at 1240 cm^{-1} is described as being due to an ester. There is no band at 1735 cm^{-1} (C=O of ester), however, which refutes the 1240 cm^{-1} assignment.

TABLE 4. SELECTED EXAMPLES OF RATIONAL, THOUGH INCORRECT, ASSIGNMENTS

<u>Band, cm⁻¹</u>	<u>Apparently erroneous assignment</u>	<u>Apparently correct assignment</u>
1715, 1690	Carbonyl	Overtone or summation bands
1710	C=O of ester	C=O of ketone
1280, 1240	C-O of aromatic alcohol	CH ₃
1235	C-O of aromatic alcohol	C-N of carbazole
1300	C-N of aryl amine	OH/C-O coupling

2. A band at 1240 cm⁻¹ is described as being due to C-O of ether. Another band at 1015 cm⁻¹, which is apparently due to symmetric stretch of C-O-C and which supports the 1240 cm⁻¹ assignment, was not utilized.
3. A band at 1590 cm⁻¹ is described as being due to an amine. This band location is typical of a primary amine, which was not indicated. Bands at 1180 cm⁻¹ and 1235 cm⁻¹, which could be the C-N stretch of a primary amine and which support the 1590 cm⁻¹ assignment, were not utilized.

3.1.3 Other Factors Affecting Accuracy of Identification

3.1.3.1 Spectroscopist Experience--

There was a correlation between accuracy of interpretation and experience of the spectroscopists, though this correlation was weak. The accuracy levels attained by spectroscopists with 25 years, 22 years, 11 years, 7 years, 3 years, and 6 months experience (one contractor had three spectroscopists involved in the study) were in the relative order 1, 3, 4, 2, 6, and 5, respectively.

3.1.3.2 Time Given to Interpretation--

The time given to interpretation of the spectra dealt with in this study ranged from 1 hour to 4 hours per spectrum, though the 4 hours included time for assignment of all IR bands to compounds already identified by LRMS. No strong correlation between accuracy of interpretation and time given to interpretation was found.

3.1.3.3 Disagreement Among Standard Sources of Band Information--

Various reference works produced by experts show disagreement regarding band assignments as is illustrated in Table 5.

TABLE 5. WAVELENGTH RANGES INDICATED FOR DIFFERENT STRUCTURES AS FOUND IN THREE DIFFERENT REFERENCE SOURCES

Structure	Reference source		
	N. B. Colthup (1950)	Dow Chemical	Nakanishi (1962)
C-O stretch of alcohol	1290-1000 cm^{-1}	1260-980 cm^{-1}	1200-1000 cm^{-1}
NH bend of primary amine	1640-1560 cm^{-1}	1665-1625 cm^{-1}	1640-1560 cm^{-1}
Aromatic C=C	1650-1550 cm^{-1} 1540-1450 cm^{-1}	1665-1615 cm^{-1} 1515-1370 cm^{-1}	1600-1450 cm^{-1} --
C-O-C of aliphatic ether	1175-1055 cm^{-1}	1140-1090 cm^{-1}	1200-1040 cm^{-1}

This variation does not lead to very many errors because the spectroscopists apparently rely more on their experience than on reference works of this sort. It has been proposed that a written guide for interpretation be prepared, which includes an assignment table for wavelength correlation with compound category. PMB-IERL/EPA is, in fact, considering preparation of such a document.

3.1.3.4 Approaches to Interpretation--

The approaches to interpretation taken by the spectroscopists are generally similar. Major bands are assigned as probably being due to certain functional or structural groups. Secondary bands are then examined, with reference works being used in this latter stage. Pattern recognition is important to some of the spectroscopists.

3.1.4 IR--Conclusions and Recommendations

In the area of IR measurements, two significant sources of error have been observed. First, the concentration of the test sample must be optimized if at all possible. Too little sample results in signals being missed and too much sample results in signal intensities being assigned incorrectly. Second, it appears that spectra acquired with KBr pellets are of relatively poor quality in the 4000 to 2000 cm^{-1} range compared with those acquired with salt plates. It is premature, however, to recommend that only salt plates be used because the data base is limited. RTI recommends that these apparent sources of error be investigated further.

Some of the errors observed arise from problems in measurement. Most arise, however, from errors in interpretation. Errors in interpretation are apparently due to unintentional oversights, incorrect information about the location of bands due to certain structures, and/or prior experiences with certain structures or compounds that have proven misleading. Such errors are best eliminated by having the spectroscopist occasionally verify his or her interpretations through the use of reference materials and/or having interpretation results occasionally checked or audited by a second, outside spectroscopist, or providing Level 1 and other EA contractors with standard assignment charts and instructional course. Other errors are the result of bias on the part of the spectroscopist, not using other bands in the spectra which would support or dispute the interpretation of the band in question, and/or not considering all reasonable interpretations of the bands in a spectrum.

These last two reasons for errors are related to a general interpretation problem--not using all available information in a spectrum. Most structures give rise to several bands in a spectrum and all should be considered when one is trying to defend or refute the presence of a particular structure. In some cases, a lone band or a group of bands will indicate two or more possible structures. All reasonable interpretations should be presented, with, if possible, some estimate of the relative amounts of these structures. One should not, however, carry this process too far and report every possible functional group for a given peak maxima. The presence or absence of confirmatory bands should dictate the final assignment(s).

The quality of the results presented by each spectroscopist is, in general, a reflection of his or her level of experience and the time given to interpretation of each spectrum, though the correlation is not strong. In fact, it is the thoroughness of the interpretation that seems to have the greatest bearing on the quality of the results. A thorough interpretation requires, however, that the spectroscopist consider all possible (and reasonable) structures that could be present in a sample. This means that the spectroscopist must have thorough training and/or a great deal of experience. Alternatively, he or she must make extensive use of reference materials. In either case, thoroughness may be expensive in terms of dollars and hours. Such thoroughness may also present a problem as the work load in the environmental assessment area increases. To deal with both the need for thoroughness in interpretation and

the increased work load, some sort of computer assistance for the spectroscopist should be considered.

3.2 LRMS STUDIES

3.2.1 LRMS Measurements

The contractors obtained low resolution mass spectra on three samples--two synthetic mixtures blended to represent Level 1 LC fractions 5 and 6, and a sample of coal tar. All samples were analyzed using a direct insertion heated probe with a series of spectra taken on a sample as the sample was being volatilized from the probe. Three out of four analysts obtained their spectra via digital readout recording systems. One analyst obtained the spectra via an analog oscillographic trace.

No differences in the quality of the spectral data obtained or in the results of the contractor's analyses of these data were found to be attributable to the instrumentation or measurement techniques used. For example, although one contractor found that spectra taken at low (15 eV) ionizing voltage was useful in the identification of molecular ions not easily disclosed from the 70-eV spectra, the other contractors did not use this approach, nor did it appear to significantly affect the overall quality of results for these three samples.

3.2.2 LRMS Interpretation

In evaluating the results, it was soon apparent that very often a category assignment was itself based on the assignment of peaks to one compound. Nevertheless, the primary goal of Level 1 environmental assessment is the identification of compound classes. Thus, for the purposes of this study, correct compound class identification is given greater significance than the identification of individual compounds although this information is also very important.

The results of both stages of the spectral interpretation test indicated that 50 to 90 percent of the compound classes present in the eight synthetic mixtures were correctly identified (Tables 6 and 7). The categories most often missed were fused ring acids, ketones, and phenols. Many individual compounds were also identified by the contractors in the test spectra (Table 8) and test samples (Table 9).

TABLE 6. CATEGORIES IN THE IR/LRMS SPECTRAL INTERPRETATION TEST CORRECTLY IDENTIFIED BY LRMS (SUM OF INTENSITIES OF COMPOUNDS IN THE CATEGORIES)

Category	mg/L	Weight %	Contractor			
			A	B	C	D
LC4a Fused alternate, nonalter- nate hydrocarbons	15,835	100.0	810	*	630	320
LC4b Fused alternate, nonalter- nate hydrocarbons	16,813	100.0	260	*	280	321
LC5a Fused alternate, nonalter- nate hydrocarbons Heterocyclic nitrogen compounds	3,016	14.0	NR	NR	20	NR
	18,584	86.0	130	*	330	231
LC5b Heterocyclic nitrogen compounds	12,105	92.2	210	*	340	110
Ketones	1,016	7.7	110	*	10	111
LC6a Heterocyclic nitrogen compound or phenol or ketone Phenol	4,214	67.9	100	NR	100	NR
	1,992	32.1	30	NR	20	NR
LC6b Ketone Phenol Ether or acid Ketone or acid Acid	2,074	22.6	NR	**($\frac{1}{2}$)	$\frac{1}{2}$	111
	1,026	11.2	100	NR	NR	NR
	2,066	22.5	NR	**($\frac{1}{2}$)	10	NR
	1,992	21.7	NR	*	100	**($\frac{1}{2}$)
	2,037	22.2	NR	*	10	NR
Total correct out of 13			8	8	114	64

NR = Not reported.

*Category identified but intensity not given. Category assignment made by RTI on the basis of contractors' data.

In each of these cases half credit was given:

**("C") category of ketone was identified but was based on 9-fluorene-4-carboxylic acid and not 9-fluorenone-4-carboxylic acid; ("B") acid category of ether or acid identified, but assignment was based on 9-fluorenone-4-carboxylic acid and not o-phenoxybenzoic acid. Also ketone category was identified but assignment was based on 9-fluorenone-4-carboxylic acid and not 9-fluorenone.

NOTE: Categories missed by all contractors: none.

TABLE 7. CATEGORIES CORRECTLY IDENTIFIED BY CONTRACTORS IN LC5 AND LC6
TEST SAMPLES BY LRMS

Category	mg/L	Weight %	Contractor			
			A	B	C	D
LC5						
Fused alternate, nonalter- nate hydrocarbons	1,748	8.6	10	NR*	20	20
Heterocyclic nitrogen compounds	17,042	83.9	110	160	430	120
Ketone	1,522	7.5	111	100	20	111
LC6						
Ketone†	7,027	41.1	200	100	30	10
Acid†	8,975	52.5	NR	40	110	NR
Phenol	1,078	6.3	NR	NR	10	10
Total correct out of 6			4	4	6	5

1) NR = Not reported.

*Although a compound belonging to this category was identified, the category itself was not listed.
†9-Fluorenone-4-carboxylic acid was placed in acid category.

TABLE 8. COMPOUNDS IN THE IR/LRMS SPECTRAL INTERPRETATION TEST CORRECTLY IDENTIFIED BY LRMS

	Compound	MW	mg/L	Weight %	Contractor			
					A	B	C	D
LC4a	Naphthalene	128	980	6.2	10	NR	10	10
	Anthracene	178	5,868	37.1	100	*	100	100
	9-Methyl anthracene	192	3,980	25.1	100	*	100	100
	Phenanthrene	178	980	6.2	100	*	100	100
	9,10-Dimethyl anthracene	206	4,027	25.4	100	*	100	10
LC4b	Naphthalene	128	5,880	35.0	10	NR	10	100
	Anthracene	178	3,920	23.3	100	*	100	100
	9-Methyl anthracene	192	986	5.9	10	*	10	100
	Phenanthrene	178	3,928	23.4	100	*	100	100
	9,10-Dimethyl anthracene	206	1,034	6.2	10	*	10	10
	2,3-Dimethyl naphthalene	156	1,065	6.3	10	NR	10	10
LC5a	Fluorene	166	1,964	9.1	NR	NR	NR	NR
	2,3-Benzofluorene	216	1,052	4.9	NR	NR	10	NR
	n-Ethyl carbazole	195	11,265	52.1	NR	NR	100	100
	2-Methyl indole	131	1,937	9.0	10	NR	10	10
	Carbazole	167	4,328	20.0	100	NR	100	100
	2,3-Dimethyl indole	145	1,054	4.9	10	NR	10	10
LC5b	7,8-Benzoquinoline	179	2,155	16.1	100	*†	100	100†
	Phenanthradine	179	4,002	30.5	100	*†	100	100†
	1,10-Phenanthroline	180	2,032	15.5	NR	NR	NR	NR
	Phenazine	180	3,956	30.2	NR	NR	100	NR
	Anthrone	194	1,016	7.7	NR	NR	NR	NR

(continued)

TABLE 8. (continued)

	Compound	MW	mg/L	Weight %	Contractor			
					A	B	C	D
LC6a	2-Hydroxy pyridine	95	4,214	67.9	100	NR	100	NR
	2,6-Dimethyl phenol	122	1,022	16.5	10	NR	10	NR
	6-6-Biphenol	186	970	15.6	10	NR	10	NR
LC6b	9-Fluorenone	180	2,074	22.6	NR	NR	NR	NR
	2,6-Dimethyl phenol	122	1,026	11.2	NR	NR	NR	NR
	o-Phenoxy benzoic acid	214	2,066	22.5	NR	NR	10	NR
	1-Fluorene carboxylic acid	210	2,037	22.2	NR	*	10	NR
	9-Fluorenone-4-carboxylic acid	224	1,992	21.7	NR	*	100	NR
Total correct out of 30					19	12	25	17

NR = Not reported.

*Compound was reported but intensity was not reported as required by Level 1.

†Credit was given for assignment of isomers of actual test spectra compounds. For example, assignment of ethyl anthracene was considered correct although dimethyl anthracene was the actual compound. Also, credit was given here for the assignment of acridine instead of 7,8-benzoquinoline and phenanthradine because all three are isomers and have nearly identical mass spectra.

NOTE: Compounds missed or incorrectly identified by all contractors: fluorene, 1,10-phenanthroline, anthrone, 9-fluorenone, and 2,6-dimethyl phenol.

TABLE 9. COMPOUNDS CORRECTLY IDENTIFIED BY CONTRACTORS IN LC5 AND LC6
TEST SAMPLES BY LRMS

	Compound	MW	mg/L	Weight %	Contractor			
					A	B	C	D
LC5	Fluorene	166	908	4.5	NR	NR	10	10
	2,3-Benzofluorene	216	840	4.1	NR	NR	10	10
	7,8-Benzoquinoline	179	3,936	19.4	100*	100*	100	100*
	1,10-Phenanthroline	180	6,294	31.0	NR	NR	10	NR
	Phenazine	180	3,405	16.8	NR	NR	100	NR
	2,6-Dimethyl quinoline	157	3,407	16.8	NR	30	100	10
	Anthrone	194	1,522	7.5	10	NR	NR	NR
LC6	9-Fluorenone	180	4,461	26.1	100	100	10	10
	1-Fluorene carboxylic acid	210	1,888	11.1	NR	NR	10	NR
	9-Fluorenone-4-carboxylic acid	224	7,087	41.5	NR	40	100	NR
	2-Methyl-1-tetralone	160	892	5.2	NR	NR	10	NR
	2-t-Butyl phenol	150	1,078	6.3	NR	NR	10	10
	2-Methyl-1,4-naphthoquinone	172	1,674	9.8	NR	NR	10	NR
Total correct out of 13					3	4	12	6

NR = Not reported.

*Phenanthradine and acridine are isomers of 7,8-benzoquinoline and were considered correct identifications here.

To distinguish differences in contractors' interpretations of the test spectra and samples and to identify sources of interpretation errors, two specific elements of the interpretation were examined. The contractors' LRMS signal assignments for the molecular ions in the spectra were compared (Tables 10 and 11) and all of the ions (molecular and fragment) assigned by the contractors to the compounds they correctly identified were compared (Tables 12 and 13). Five types of LRMS interpretation errors were observed.

The five types of LRMS interpretation errors observed in the results from the spectral interpretation test spectra and samples are:

1. Errors of omission--not noting the presence of molecular ions.
2. Reporting molecular ions as fragment ions.
3. Reporting fragment ions as molecular ions.
4. Incorrectly identifying molecular ions.
5. Incorrectly assigning ions to a homologous series.

Failure to find molecular ions accounted for almost half the categories and compounds missed in the test spectra and mixtures (Table 14).

In general, the contractors' category assignments for compounds identified in the tar sample were consistent with those expected to elute in these fractions as well as in fair agreement with results from a limited analysis of the sample by capillary column gas chromatography/mass spectrometry (Tables 15 and 16). Significant carryover of fused alternate hydrocarbons from earlier fractions was observed by Contractor A. Some disparity in the extent of spectral interpretation is evident if the molecular weight ranges reported by the contractors are examined (Table 17). The somewhat higher mass ranges reported by Contractor A were due primarily to the influence of higher molecular weight compounds carried over from fractions 2 and 3. Contractor C's narrow range of masses reported for fraction 6 was found to be due to analysts failing to report data for the probe inlet spectrum of this fraction. The compounds reported were those detected by batch inlet. Contractor B did not interpret the tar sample spectra very carefully.

In general, signal assignments (Table 18) were based on molecular ions only with supportive evidence given by the finding of other members of an alkylated homologous series. It is difficult to determine solely on the basis of the tabulated data which identifications are justified and which are not because many of the series overlap.

TABLE 10. CONTRACTORS' LRMS SIGNAL ASSIGNMENTS FOR SPECIFIC MOLECULAR IONS IN THE LRMS TEST SPECTRA

Fraction	Ion	Expected	Contractor			
			A	B	C	D
LC4a	128	Naphthalene	Naphthalene	NA	Naphthalene	Naphthalene
	178	Anthracene, phenanthrene	Anthracene, phenanthrene	Anthracene, phenanthrene	Anthracene or phenanthrene	Anthracene or isomer
	192	9-Methyl anthracene	Methyl anthracene or methyl phenanthrene	Methyl anthracene	Methyl anthracene or methyl phenanthrene	Methyl anthracene or isomer
	206	9,10-Dimethyl anthracene	Dimethyl anthracene or phenanthrene	Dimethyl- or ethyl anthracene or phenanthrene	Dimethyl anthracene or dimethyl phenanthrene	Ethyl anthracene or isomer
LC4b	128	Naphthalene	Naphthalene	NA	Naphthalene	Naphthalene
	178	Anthracene, phenanthrene	Anthracene, phenanthrene	Anthracene, phenanthrene	Anthracene or phenanthrene	Anthracene or isomer
	192	9-Methyl anthracene	Methyl anthracene or phenanthrene	Methyl anthracene	Methyl anthracene or phenanthrene	Methyl anthracene or isomer
	206	9,10-Dimethyl anthracene	Dimethyl anthracene or phenanthrene	Dimethyl- or ethyl anthracene or phenanthrene	Ethyl anthracene or ethyl phenanthrene or dimethyl anthracene or dimethyl phenanthrene	Ethyl anthracene or isomer
LC5a	156	2,3-Dimethyl naphthalene	Dimethyl naphthalene	NA	Dimethyl naphthalene	Dimethyl naphthalene
	166	Fluorene	Fragment of phenanthridone, carbazole, methyl carbazole	NA	Fragment of carbazole, ethyl carbazole, or dimethyl carbazole	NA
	216	2,3-Benzofluorene	Unidentified	NA	Methyl pyrene or benzofluorene	NA
	195	n-Ethyl carbazole	Phenanthridone, acridone	Acridone	Ethyl carbazole or dimethyl carbazole	Ethyl carbazole
	131	2-Methyl indole	Methyl indole	NA	Methyl indole	Methyl indole
	167	Carbazole	Carbazole	Acridone fragment ion	Carbazole	Carbazole
	145	2,3-Dimethyl indole	Dimethyl indole	NA	Dimethyl indole	Ethyl indole

(continued)

TABLE 10. (continued)

Fraction	Ion	Expected	Contractor			
			A	B	C	D
LC5b	179	7,8-Benzoquinoline, phenanthradine	Benzoquinoline, phen- anthradine	Acridine	7,8-Benzoquinoline or phenanthridine	Acridine
	180	1,10-Phenanthroline; phenazine	Fluorenone	Fluorenone	Phenazine, fragment of anthraquinone or dimethyl benzo[c]cin- noline	Fluorenone
	194	Anthrone	Methyl fluorenone	Methyl fluorenone	Methyl benzoquinoline or methyl benzo[c]- cinnoline	Methyl fluorenone
LC6a	95	2-Hydroxy pyridine	Hydroxy pyridine Cresol, ethyl phenol Biphenylidol (6,6'-biphenol)	NA	2-Pyridone	Phenyl ether fragment
	122	2,6-Dimethyl phenol		NA	Dimethyl phenol	Phenyl ether fragment
	186	6,6'-Biphenol		NA	6,6'-Biphenol	Phenyl ether
LC6b	180	9-Fluorenone	NA	NA	NA	NA
	122	2,6-Dimethyl phenol	NA	NA	o-Phenoxy benzoic acid fragment	NA
	214	o-Phenoxy benzoic acid	NA	NA	o-phenoxy benzoic acid	NA
23	210	1-Fluorene carboxylic acid	NA	Carboxy fluorene	Fluorene carboxylic acid	Methyl xanthone
	224	9-Fluorenone-4-carbox- ylic acid	Hydroxyanthraquinone	Carboxy fluorenone or carboxy methyl fluo- rene	9-Fluorenone-4-carbox- ylic acid	Dimethyl or ethyl xanthone

NA = Not assigned.

TABLE 11. CONTRACTORS LRMS SIGNAL ASSIGNMENTS FOR SPECIFIC MOLECULAR IONS IN THE LOW RESOLUTION MASS SPECTRA THEY GENERATED FROM THE TEST MIXTURES

Fraction	Ion	Expected	Contractor			
			A	B	C	D
LC5	166	Fluorene	NA	NA	Fluorene, fragment of methyl phenanthroline or methyl benzo[c]cinoline	Fluorene
	216	2,3-Benzofluorene	Methyl pyrene	NA	2,3-Benzofluorene or methyl pyrene	Benzofluorene
	179	7,8-Benzoquinoline	Acridine, phenanthridine, etc.	Acridine	Benzofluorene, acridine; phenazine and 1,10-phenanthroline fragment	Acridine
	180	1,1-Phenanthroline, phenazine	Fluorenone	Fluorenone or methylfluorene	Phenazine, 1,10-phenanthroline, anthraquinone fragment	Fluorenone
	157	2,6-Dimethyl quinoline	NA	Dimethyl quinoline	Dimethyl quinoline	Dimethyl or ethyl quinoline
	194	Anthrone	Anthrone	NA	Methyl phenanthroline or methyl benzo[c]cinoline; fragment of methyl benzoquinoline or beta-naphthaquinoline	Methyl fluorenone
	180	9-Fluorenone	Fluorenone	Fluorenone	Fluorenone or 1-phenalene	Fluorenone
LC6	210	1-Fluorene carboxylic acid	Unknown	NA	Fluorene carboxylic acid	NA
	224	9-Fluorenone-4-carboxylic acid	Hydroxy anthraquinone	Carboxy fluorenone	9-Fluorenone-4-carboxylic acid	NA
	160	2-Methyl-1-tetralone	NA	NA	Methyl tetralone	NA
	150	2-t-Butyl phenol	Fluorenone fragment	NA	t-Butyl phenol; fragment of fluorenone or 1-phenalene; fragment of 9-fluorenone-4-carboxylic acid	t-Butyl phenol
	172	2-Methyl-1,4-naphthoquinone	Ethoxy naphthalene	NA	Methyl naphthoquinone	NA

NA = Not assigned.

TABLE 12. LRMS SIGNAL ASSIGNMENTS FOR COMPOUNDS IN THE SPECTRAL INTERPRETATION TEST SPECTRA

	Compound	MW	Weight %	Contractor			
				A	B	C	D
LC4a	Naphthalene	128	6.2	128	NR	128,127,129,64, 51,126,102,63	128
	Anthracene	178	37.1	178,179,176,89, 152,151,150,177	178	178,176,179,89, 76,88,151,152	178
	9-Methyl anthracene	192	25.1	192,191,189,193, 94.5	192,206,191	192,191,189,193, 94.5,96,82.5,190	192
	Phenanthrene	178	6.2	178,179,176,89, 152,151,150,177	178	178,176,179,89, 76,88,151,152	178
	9,10-Dimethyl anthracene	206	25.4	206,191,205,207, 189,165,202,203, 204	192,206,191	206,191,207,189, 89,192,101,82.5	206
LC4b	Naphthalene	128	35.0	128	NR	128,127,129,64, 51,126,102,63	128
	Anthracene	178	23.3	178,179,176,89, 152,151,150	178	178,179,176,89, 177,152,151,76	178
	9-Methyl anthracene	192	5.9	192,191,189,193, 94.5	192,206	192,191,189,193, 94.5,96,82.5,190	192
	Phenanthrene	178	23.4	178,179,176,89, 152,151,150,177	178	178,179,176,89, 177,152,151,76	178
	9,10-Dimethyl anthracene	206	6.2	206,191,205,189, 202,203,204,207, 165	192,206	206,191,207,189, 89,192,101,82.5	206
	2,3-Dimethyl naphthalene	156	6.3	156,141	NR	156,141,155,115, 157,142,76,153	156
LC5a	Fluorene	166	9.1	NR	NR	NR	NR
	2,3-Benzofluorene	216	4.9	NR	NR	216,215,94.5,217, 108,213,202,107.5	NR

(continued)

TABLE 12. (continued)

	Compound	MW	Weight %	Contractor			D*
				A	B	C	
LC5a (con.)	n-Ethyl carbazole	195	52.1	NR	NR	180,195,152,166, 140,139,151,196	195
	2-Methylindole	131	9.0	130,131	NR	130,131,65,77,51, 103,78,102	131
	Carbazole	167	20.0	167,166,139	NR	167,166,168,83.5, 139,63,69.5	167
	2,3-Dimethylindole	145	4.9	144,145	NR	144,145,130,143, 77,115,146,103	145
LC5b	7,8-Benzoquinoline	179	16.1	179,150,151,152, 153	NR	179,178,180,89.5, 151,76,89,152	NR
	Phenanthradine	179	30.5	179,150,151,152, 153	NR	179,178,180,89.5, 151,76,89,152	NR
	1,10-Phenanthroline	180	15.5	NR	NR	NR	NR
	Phenazine	180	30.2	NR	NR	180,179,90,76, 153,128,63,154	NR
LC6a	Anthrone	194	7.7	NR	NR	NR	NR
	2-Hydroxy pyridine	95	67.9	95,67,41,51	NR	95,67,41,66	NR
	2,6-Dimethyl phenol	122	16.5	122,107,77,51	NR	122,107,121,77, 51,79,91	NR
	6-6-8iphenol	186	15.6	186,157,158,131, 139,128,129,127	NR	186,157,158,131, 187,139,128,185	NR
	9-Fluorenone	180	22.6	NR	NR	NR	NR
	2,6-Dimethyl phenol	122	11.2	NR	NR	NR	NR
	0-Phenoxybenzoic acid	214	22.5	NR	NR	121,214,51,77, 65,120,122	NR
	1-Fluorene carboxylic acid	210	22.2	NR	210,165	165,210,166	NR
	9-Fluorenone-4-carboxylic acid	224	21.7	NR	224,179	224,225,207,151, 179,152,139	NR

*0⁰ listed fragment ions for all compounds reported. Thus, the corresponding fragments could not be differentiated.

TABLE 13. LRMS SIGNAL ASSIGNMENTS FOR COMPOUNDS IN THE SPECTRAL INTERPRETATION TEST MIXTURES

	Compound	MW	Weight %	Contractor			
				A	B	C	D
LC5	Fluorene	166	4.5	NR	NR	166, 165, 82.5, 167 163, 83, 164, 82	166
	2,3-Benzofluorene	216	4.1	NR	NR	216, 215, 217, 94.5, 108, 107.5, 213, 106.5	216
	7,8-Benzoquinoline	179	19.4	179, 151, 89	NR	179, 178, 89.5, 151, 76, 89, 152	179
	1,10-Phenanthroline	180	31.0	NR	NR	180, 179, 154, 153, 128, 90, 76, 63	NR
	Phenazine	180	16.8	NR	NR	180, 179, 154, 153, 128, 90, 76, 63	NR
LC6	2,6-Dimethyl quinoline	157	16.8	NR	157	157, 115, 142, 39, 51, 63	157
	Anthrone	194	7.5	193, 194	NR	NR	NR
	9-Fluorenone	180	26.1	180, 152, 151, 150, 76, 75	180	180, 152, 151, 150, 126, 76, 63, 51, 50	180
	1-Fluorene carboxylic acid	210	11.1	NR	NR	210, 166, 165	NR
	9-Fluorenone-4-carboxylic acid	224	41.5	NR	224	224, 207, 196, 179, 168, 151, 150, 139	NR
	2-Methyl-1-tetralone	160	5.2	NR	NR	160, 145, 131, 118, 90, 39	NR
	2-t-Butyl phenol	150	6.3	NR	NR	150, 135, 107, 91, 77, 39	150
	2-Methyl-1,4-naphthoquinone	172	9.8	NR	NR	172, 144, 116, 115, 104	NR

NR = Not reported.

TABLE 14. ERRORS MADE BY CONTRACTORS IN INTERPRETING
LOW RESOLUTION MASS SPECTRA THEY GENERATED FROM
TEST SAMPLES LC5 AND LC6

		Contractor				Total
	Test mixture	A	B	C	D	
1. Did not find molecular ion at all.	LC5	2	3	0	0	3
	LC6	2	4	0	4	9
2. Found molecular ion but left unidentified.	LC5	0	0	0	0	0
	LC6	1	0	0	0	1
3. Found molecular ion but identified compound incorrectly (either as fragment or as another compound).	LC5	3	2	1	3	8
	LC6	2	0	0	0	2
		10	9	1	7	23

TABLE 15. CATEGORIES REPORTED BY CONTRACTORS IN COAL
GASIFICATION FOR SAMPLE

Category	Sum of compound intensities			
	Contractor			
	A	B	C	D
LC4				
Heterocyclic nitrogen compounds	230	NR	160	300
Fused alternate, non-alternate hydrocarbons	70	NR	NR	NR
Unclassified	60	NR	NR	NR
Aliphatic hydrocarbons	NR	*	NR	NR
Phenols	NR	NR	NR	200
LC5				
Aromatic nitrile	NR	NR	100	NR
Heterocyclic sulfur	NR	NR	30	NR
Phenols	110	NR	210	220
Ketones	200	NR	NR	40
Aliphatic hydrocarbons	NR	*	NR	NR
Unclassified	10	NR	NR	20
LC6				
Phenols	340	100	310	NR
Heterocyclic nitrogen compounds	60	NR	NR	510
Ketones	10	NR	NR	NR
Unclassified	10	NR	NR	10

NR = Not reported.

*Compound was reported but intensity was not reported as required by Level 1.

TABLE 16. COMPOUNDS FOUND IN TAR SAMPLE BY GC/MS AND
REPORTED BY CONTRACTOR

Category	Compounds	Contractor			
		A	B	C	C
Fused alternate, nonalternate hydrocarbons	Naphthalene	---	---	---	---
	2-Methyl naphthalene	---	---	---	---
	1-Methyl naphthalene	---	---	---	---
	C ₂ -naphthalenes	---	---	---	---
	Biphenyl	---	---	---	---
	Acenaphthylene	---	---	---	---
	Acenaphthene	---	---	---	---
	Fluorene	---	---	---	---
	Phenanthrene	---	---	---	---
	Anthracene	---	---	---	---
	Fluoranthene	10	---	---	---
	Pyrene	10	---	---	---
	Benzo(a)fluorene	---	---	---	---
	Benzo(b)fluorene	---	---	---	---
	Benzo(a)anthracene	10	---	---	---
	Chrysene + triphenylene	10	---	---	---
	Benzo(b)fluoranthene	---	---	---	---
	Benzo(e)pyrene	10	---	---	---
	Benzo(a)pyrene	10	---	---	---
	Perylene	10	---	---	---
	Dibenzo(a,h)anthracene	---	---	---	---
	Indeno(1,2,3-Cd)pyrene	---	---	---	---
	Benzo(g,h,i)perylene	10	---	---	---
Heterocyclic sulfur compounds	Benzothiophene	---	---	10	---
Heterocyclic oxygen compounds	Dibenzofuran	100	---	---	---
Heterocyclic nitrogen compounds	Carbazole	100	---	100	100
	Benzidine	---	---	---	---
	Alkyl pyridines	---	---	---	100
	Quinoline	10	---	---	100
	Alkylquinolines	10	---	---	100
	Alkyl benzoquinolines	---	---	---	---
	Acridine	10	---	---	100
Phenols	Phenol	100	---	100	100
	Cresols	100	---	100	---
	Xylenols	100	100	100	---
	o-Isopropylphenols	---	---	10	---
	Trimethyl phenol	---	---	10	---
	Number agreeing with GC data excluding fused alternate, nonalternate hydro- carbons	8	1	7	6

TABLE 17. MOLECULAR WEIGHT RANGES REPORTED BY CONTRACTORS FOR COAL GASIFICATION TAR SAMPLE

	Contractor			
	A	B	C	D
LC4	167-500	43-91	167-231	167-195
LC5	100-252	43-91	128-212	108-252
LC6	94-300	122	94-136	79-217

TABLE 18. LRMS SIGNAL ASSIGNMENTS FOR SELECTED COMPOUNDS REPORTED BY CONTRACTORS IN THE COAL GASIFICATION TAR SAMPLE

Compound	MW	Contractor			
		A	B	C	D
LC4					
Carbazole	167	167	NA, P	167, 166, 139, 83.5, 69.5	167, P
Dibenzocarbazole	267	267	NA, P	63, 39, 267	NA, NP
Naphthol	144	144	NA, P	NA	144
LC5					
Methyl naphthol	158	158	NA, NP	158, 157, 115, 129, 128, 127	158
LC6					
Phenol	94	94	NA, P	94, 39, 66, 65	NA, P
Cresol	108	108	NA, P	108, 107, 77, 79, 51, 39	NA, P
Ethyl/dimethyl phenol	122	122	122, 107, 94, 77	122, 107, 121, 39, 77, 51, 79	NA, P
Acridine	179	179	NA, P	NA, P	179
Quinoline	129	129	NA, P	NA, P	129
Pyridine	79	NA, P	NA, P	NA, P	79

NA = Not assigned.

NP = Not present in spectra.

P = Present in spectra.

Factors other than errors in assignment and errors of omission that affect analysis accuracy include the approach to interpretation taken and the degree of interaction with the IR analyst to produce a composite report on the sample. The analyst's experience (years spent as a mass spectroscopist) and the time given to interpretation had little bearing on the results. A composite list of the major factors that correlate either positively or negatively with the more successful spectral interpretations include as positive correlates the search for molecular ions, the search for the eight most abundant fragment ions, the setting of intensity and mass/charge range criteria for peaks to be studied in a spectrum, the use of the tabulated reference source, the Eight Peak Index of Mass Spectra (Imperial Chemical Industry), and the careful consideration of the IR data analyses in making final compound class/compound assignments (Table 19). Excessive dependence on the LC fraction number as a determining factor for accepting or rejecting compounds and compound classes was found to be a problem for several contractors.

It is not impossible for compounds from one category to be observed to elute over as many as four LC fractions. However, the majority of the compounds from this category should still be observed in the correct LC fraction. Also, individual compounds in general should elute within ± 1 fraction of the expected. Usually, if an individual compound is observed in more than three LC fractions, i.e., the expected and those on either side, then either the compound identification is wrong or the LC separation is unsatisfactory. The only case where such an elution would be expected is if the great majority of the sample loaded onto the column is one compound (e.g., 50 mg of anthracene). Needless to say this seldom occurs in real assessment samples. So, although the LC separation data are generally very useful for delineating the presence of individual compounds, they should still be used with caution to evaluate the presence or absence of compound classes. After reviewing the IR interpretation results, the LRMS analysts in many cases revised their observations by adding new categories and/or compounds and by confirming or rejecting the presence of those already listed based on the LRMS alone (Table 20). In nearly every case these changes enhanced the quality of the data.

3.2.3 LRMS Recommendations

Five recommendations regarding LRMS measurement and spectral interpretation have been developed. These are:

TABLE 19. LOW RESOLUTION MASS SPECTRAL INTERPRETATION DATA
INPUTS AND HOW THEY ARE USED BY CONTRACTORS*

	Contractor			
	A	B	C	D
1. Looks for molecular ions	✓	✓	✓	✓
2. Looks for some fragment ions	✓	✓	✓	✓
3. Looks for eight most abundant ions	✓	✓	✓	✓
4. Accounts for all peaks above given intensity and m/e value	✓	✓	✓	most peaks
5. Finding homologous series very important	✓	✓	no	✓
6. Peak intensity ratios	✓	✓	no	✓
7. IR data given equal weight	no	no	no	no
8. LC data used to verify & exclude	✓	✓	no	✓
9. LC data used to verify only	no	no	✓	no
10. Eight-peak Index used often	✓	no	✓	✓

✓ = agrees with input shown.

No = does not agree with input shown.

*NOTE: While this list of inputs is in agreement with the approaches described by the contractors in their communications with the study coordinator, the application of these inputs to the study spectra and samples deviated from the above, especially for Contractors B and D.

TABLE 20. CHANGES MADE IN LRMS INTERPRETATIONS BY THE LRMS ANALYST
AFTER SEEING IR INTERPRETATIONS

Sample	"A"	"B"	"C"	"D"
(1) Test spectra LC4a	NC	NC	Anthracene major component Phenanthrene <u>minor</u> component Dimethylanthracene <u>major</u> component	NC
LC4b	NC	NC	Anthracene, phenanthrene <u>same amounts</u>	NC
LC5a	NC	Acridone and fluorenone were changed to carbazole and ethyl carbazole	Carbazole <u>confirmed</u> Ethyl carbazole <u>confirmed</u>	NC
LC5b	NC	NC	Benzoquinoline favored over phenanthradine Phenazine <u>major</u> component Anthraquinone	Acridine, fluorenone added
LC6a	NC	Pyridone or pyridinol, pyrrole were listed; previously nothing	Pyridone <u>confirmed</u>	Anthraquinone, 2-hydroxyanthraquinone added
LC6b	NC	NC	9-Fluorenone-4-carboxylic acid <u>major</u> component	NC
(2) Test mixtures LC5	(1) Changed fluorenone to benzocinnoline (2) Deleted anthrone due to poor IR match	NC	1,10-Phenanthroline <u>minor</u> Phenazine <u>major</u> Acridine <u>minor</u> 7,8-Benzoquinoline <u>minor</u> Anthraquinone <u>minor</u> 2,6-Dimethylquinoline <u>minor</u>	IR added but reason not given
LC6	Changed hydroxyanthraquinone to 9-fluorenone-4-carboxylic acid Added fluorene carboxylic acid	Carboxyfluorenone changed to 9-fluorenone-4-carboxylic acid	9-Fluorenone, instead of just "fluorenone" 9-Fluorenone-4-COOH <u>major</u>	Added aromatic acids

(continued)

1. Low (15 eV) ionizing voltage can be used to aid in the identification of molecular ions although this is not essential. It is especially useful if the 70-eV spectrum is not simple enough to interpret.
2. Analysts who do not have the instrumental capability to switch from 70 eV to 15 eV during a run should be allowed to use chemical ionization (CI) mass spectrometry if and only if it can be established that CI provides significantly more information on molecular ions than 70-eV EI spectra.
3. The Eight Peak Index of Mass Spectra must be used to interpret and verify spectra. Other reference sources such as the EPA/NIH Data Base (Heller and Milne), The Mass Spectral Correlation Tables, and the American Petroleum Institute Index are useful for certain cases but, as general references, they tend to be less complete or inaccurate.
4. Peak intensity and m/e range criteria must be set above which all ions will be as fully accounted for as possible. These criteria may vary from sample to sample and spectrum to spectrum.
5. A series of spectra should be obtained as a sample is being volatilized from the probe. The spectra should be examined individually as well as in relation to each other.

In addition, several recommendations have been developed that apply to both IR and LRMS techniques. These are:

1. The LC fraction table in the Level 1 Manual or any other such similarly constructed table should not be used to exclude the presence of any category. Such a table should only be used as a very rough guide to verify the presence of a category or compound already indicated on the basis of more reliable factors such as IR and LRMS data.
2. The IR and LRMS analysts should first analyze their data independently and then consult with one another to produce a composite report. Irreconcilable differences should be noted and both categories identified should be reported if the differences cannot be resolved.
3. Analysts should adhere rigidly to the nomenclature for categories given in Table 17 in the Level 1 Manual. Nomenclature for compound identification must be uniform and not based on personal preferences. The International Union of Pure and Applied Chemists nomenclature for compounds should be used by all contractors.
4. All LRMS and IR data should be reported on the Level 1 forms exactly as specified.
5. Contractors should familiarize themselves with the same source they are studying and the chemistry, if any, taking place. Under

no circumstances should the analysts limit themselves to a "list of compounds" they feel will probably be present.

6. In general, the LRMS and IR data should be used as primary data inputs to sample interpretation. Other inputs, such as LC fraction, sample source, and previously generated data on similar sources, should be given less weight.
7. Polyfunctional compounds like fluorenone-4-carboxylic acid should be listed as both possible categories (in this case, acid and ketone). Quantitation in such cases should be investigated.
8. All contractors performing Level 1 LRMS and IR analyses should be given the opportunity to complete spectral interpretation tests that will measure the contractor's analytical and interpretive abilities on appropriate real and synthetic test samples. To relate the test results to actual sample analyses, these tests must have cost/time considerations. For example, the contractor should spend "X" hours and should prepare the sample(s) "Y" number of times. Some idea must be given of the intensity of the application of the technique.
9. In conjunction with 8, all contractors performing Level 1 LRMS and IR analyses should receive guidelines documents illustrating efficient and accurate ways in which Level 1 LRMS and IR can be performed. These guidelines should contain numerous completely worked out example spectra. Also, along with these training sets, workshops should be held during which Level 1 LRMS and IR experts will interact and exchange ideas.

Implementation of Steps 1 through 9 will improve the quality of the data generated by contractors now performing Level 1 LRMS and IR as well as aid those laboratories just beginning Level 1 work.

SECTION 4

PREPARATION OF TEST SPECTRA AND SAMPLES

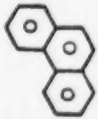
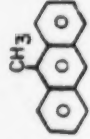
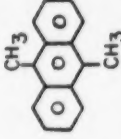
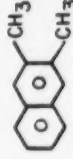
4.1 CHOICE OF COMPOUNDS

Level 1 LC fractions 4, 5, and 6 have always presented the greatest challenges to the IR and LRMS methodologies. For this reason, the classes or categories of compounds found in these fractions were chosen to be the focus of this study. The compounds with which to prepare the test spectra and test mixtures were selected both on the basis of classes of compounds expected to elute in these fractions and compounds reported in these fractions in actual environmental assessment studies. Thus, while fused alternate-nonalternate hydrocarbons like anthracene and benzofluorene would be predicted to elute in LC fraction 2 according to the Level 1 manual, published data from several environmental assessments show the presence of these types of compounds in higher LC fractions. Hence, for the purposes of this study, compounds from these compound classes (fused alternate-nonalternate hydrocarbons) were included in fractions 4 and 5.

Two test spectra were prepared for each LC fraction; one spectrum was intended to be more difficult to interpret than the other. The concentrations of the compounds in the mixtures used to prepare these spectra were reasonably high so that problems of detection would not be a factor and would not interfere with studies of the measurement and interpretation components of the IR/LRMS analyses. These same criteria were followed in preparation of the two test mixtures. The compounds in the mixtures used to prepare the test spectra and the compounds in the test mixtures are listed in Tables 21 and 22.

The coal gasification tar sample was provided by Dr. Santosh Gangwal (RTI). This sample was included in the study to determine what differences in approach to measurement and interpretation would result with a real sample.

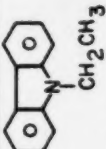
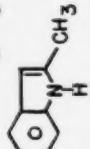
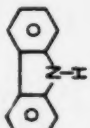
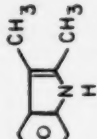
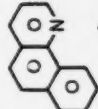
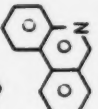
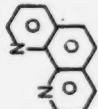
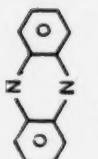
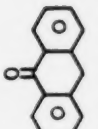
TABLE 21. COMPOSITION OF MIXTURES USED TO GENERATE TEST SPECTRA

Compound	MEG category*	Structure	MW	mg/L		Weight (%)	
				$\frac{a}{980}$	$\frac{b}{5,880}$	$\frac{a}{6.2}$	$\frac{b}{35.0}$
LC4a,b Naphthalene	21		128				
Anthracene	21		178	5,868	3,920	37.1	23.3
Phenanthrene	21		178	980	3,928	6.2	23.4
9-Methyl anthracene	21		192	3,980	986	25.1	5.9
9,10-Dimethyl anthracene	21		206	4,027	1,034	25.4	6.2
2,3-Dimethyl naphthalene	21		156	0	1,065	0	6.3
LC5a Fluorene	22		166	1,964		9.1	
2,3-Benzofluorene	22		216	1,052		4.9	

*See footnote at end of table.

(continued)

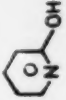
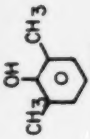
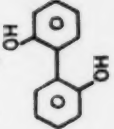
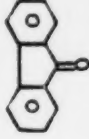
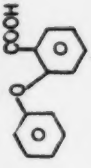
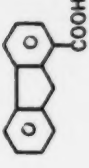
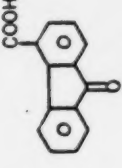
TABLE 21. (continued)

Compound	MEG category*	Structure	MW	mg/L	Weight (%)
n-Ethyl carbazole	23		195	11,265	52.1
2-Methyl indole	23		131	1,937	9.0
Carbazole	23		167	4,328	20.0
2,3-Dimethyl indole	23		145	1,054	4.9
LC5b 7,8-Benzoquinoline	23		179	2,115	16.1
Phenanthradine	23		179	4,002	30.5
1,10-Phenanthroline	23		180	2,032	15.5
Phenazine	23		180	3,956	30.2
Anthrone	7		194	1,016	7.7

*See footnote at end of table.

(continued)

TABLE 21. (continued)

Compound	MEG category*	Structure	MW	mg/L	Weight (%)
LC6a 2-Hydroxypyridine	23		95	4,214	67.9
2,6-Dimethyl phenol	18		122	$\frac{a}{1,022}$ $\frac{b}{1,026}$	$\frac{a}{16.5}$ $\frac{a}{11.2}$
o-o-Biphenol	18		186	970	15.6
LC6b 9-Fluorenone	7 (22)		180	2,074	22.6
o-Phenoxybenzoic acid	3 (8)		214	2,066	22.5
1-Fluorene carboxylic acid	22 (8)		210	2,037	22.2
9-Fluorenone-4-carboxylic acid	7 (8)		224	1,992	21.7
2,6-Dimethyl phenol	18	(See LC6a)	122	$\frac{a}{1,022}$ $\frac{b}{1,026}$	$\frac{a}{16.5}$ $\frac{b}{11.2}$

*From Multimedia Environmental Goals for Environmental Assessment, Volume II. MEG Charts and Background Information, J. G. Cleland and G. L. Kingsbury, EPA-600/7-77-136b, November 1977.

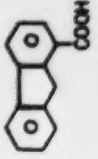
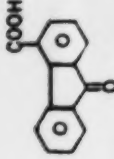
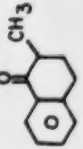
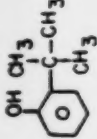
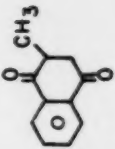
TABLE 22. COMPOSITION OF TEST MIXTURES LC5 AND LC6

Compound	MEG category*	Structure	MW	mg/L	Weight (%)
LC5 Fluorene	22		166	908	4.5
2,3-Benzofluorene	22		216	840	4.1
7,8-Benzoquinoline	23		179	3,936	19.4
1,10-Phenanthroline	23		180	6,294	31.9
Phenazine	23		180	3,405	16.8
2,6-Dimethyl quinoline	23		157	3,407	16.8
Anthrone	7		194	1,522	7.5
LC6 9-Fluorenone	7		180	4,461	26.1

(continued)

*See footnote at end of table.

TABLE 22. (continued)

Compound	MEG category*	Structure	MW	mg/L	Weight (%)
1-Fluorene carboxylic acid	22 (8)		210	1,888	11.1
9-Fluorenone-4-carboxylic acid	7 (8)		224	7,087	41.5
2-Methyl-1-tetralone	7		160	892	5.2
2-t-Butyl phenol	18		150	1,078	6.3
2-Methyl-1,4-naphthoquinone	7		172	1,674	9.8

*From Multimedia Environmental Goals for Environmental Assessment, Volume II. MEG Charts and Background Information, J. G. Cleland and G. L. Kingsbury, EPA-600/7-77-136b, November 1977.

4.2 GENERATION AND VERIFICATION OF TEST SPECTRA

4.2.1 Preparation of Mixtures

The six synthetic mixtures, designated LC4a, LC4b, LC5a, LC5b, LC6a, and LC6b, were prepared by dissolving known quantities of the mixture compounds in acetone in volumetric flasks. All compounds were completely soluble except for anthracene, which was not completely soluble in mixture LC4a. The compounds chosen to make the mixtures were obtained from Aldrich Chemical Company and were used without further purification. All were at least 97 percent pure.

4.2.2 Generation and Verification of Low Resolution Mass Spectra

Low resolution mass spectra of the six synthetic mixtures were generated by direct probe introduction of the mixtures into a VG-Micromass 70.70F mass spectrometer operated at a resolving power of 3,000. The samples were scanned repetitively at 5 sec/decade from m/e 650 to 22. The samples were ionized by electron impact using 70-eV electrons with a 200- μ A trap current and a source temperature of 200° C. Data acquisition and reduction were by means of a VG 2035 data system. The output used by RTI for each mixture consisted of a single spectrum, single ion plots for the molecular ions for each compound and a listing of the masses and intensities for all ions recorded. Under the conditions employed, the molecular ion for nearly every compound was a maximum according to the total ion current monitored for each expected molecular ion (Table 23). The four participating contractors were sent only the test spectrum for each mixture along with the designated report forms.

The test spectra were verified by searching the spectra for the eight most abundant ions for each mixture compound as listed in the Eight Peak Index of Mass Spectra (Imperial Chemical Industry). All compounds in the mixtures that were listed in this reference were so verified. Four compounds--9-methyl anthracene, 9,10-dimethyl anthracene, phenanthradine, and 1-fluorene carboxylic acid--were not listed and could not be verified. Eight Peak Index listings for 9-methyl phenanthrene and 9,10-dimethyl phenanthrene were searched for and verified. This tends to confirm the presence of the anthracene analogs because anthracene and phenanthrene are isomers with nearly identical low resolution mass spectra. Because phenanthradine and 7,8-benzoquinoline are isomers and are unlikely to undergo extensive fragmentation, it was assumed

TABLE 23. SUMMARY OF SINGLE ION PLOTS RECORDED FOR TEST SPECTRA

Compound	Molecular ion	Percent intensity of maximum ion current
LC4a		
Naphthalene	128	100
Anthracene	178	100
9-Methylanthracene	192	100
Phenanthrene	178	100
9,10-Dimethyl anthracene	206	100
LC4b		
Naphthalene	128	35
Anthracene	178	100
9-Methylanthracene	192	60
Phenanthrene	178	100
9,10-Dimethyl anthracene	206	20
2,3-Dimethyl naphthalene	156	30
LC5a		
Fluorene	166	88
2,3-Benzofluorene	216	22
n-Ethyl carbazole	195	100
2-Methyl indole	131	88
Carbazole	167	85
2,3-Dimethyl indole	145	90
LC5b		
7,8-Benzoquinoline	179	100
Phenanthradine	179	100
1,10-Phenanthroline	180	95
Phenazine	180	95
Anthrone	194	100
LC6a		
2-Hydroxy pyridine	95	100
2,6-Dimethyl phenol	122	100
o-6-Biphenol	186	100
LC6b		
9-Fluorenone	180	8
2,6-Dimethyl phenol	122	8
O-Phenoxybenzoic acid	214	5
1-Fluorene-carboxylic acid	210	100
9-Fluorenone-4-carboxylic acid	224	100

that their mass spectra would be nearly identical. The compounds in the test spectra mixtures are shown in Table 24 along with the eight most abundant peaks used to verify the compounds. Also shown are the percent intensities for these eight peaks relative to the base peak for the pure compound and for the compound as it appears in the mixture spectra.

4.2.3 Generation and Verification of Infrared Spectra

Infrared spectra of the six synthetic mixtures were generated by slurring aliquots of each mixture with approximately 300 mg of IR grade KBr. These slurries were allowed to go to dryness in a desiccator. Next, 13-mm KBr pellets were prepared from the dried mixtures and IR spectra were obtained with a Perkin-Elmer 467 grating spectrophotometer using the medium scan-mode, the normal slit program, and a time constant of 2.

The presence of the mixture compounds was verified by searching each of the six spectra for the characteristic bands of each compound as found in the Sadtler Index spectra (Sadtler Research Laboratories) for the pure compounds. Nearly all of the significant bands as well as many of the minor bands were present for all mixture compounds (see Appendix A). The four participating contractors were sent only the test spectra and the designated forms. A band appearing in nearly all of the spectra at around $2560\text{--}2580\text{ cm}^{-1}$ was determined to be an instrumental artifact. The contractors were not informed of this artifact band in order to test their interpretation of such bands.

4.3 GENERATION AND VERIFICATION OF SYNTHETIC TEST MIXTURES

4.3.1 Preparation of Mixtures

Based on the results reported by the four contractors for the test spectra, two synthetic test mixtures designated LC5 and LC6 were prepared gravimetrically in acetone. Most of the test mixture compounds were those compounds in the test spectra identified incorrectly or not identified by at least three out of four contractors. Thus, for these contractors, these test mixtures would present a greater challenge than the mixtures used to generate the stage one spectra although they still contain similar or the same compound classes included in stage one. All of the compounds were completely soluble. Acetone blanks were also sent along with the samples.

TABLE 24. VERIFICATION OF LOW RESOLUTION TEST SPECTRA

	MW	Eight most abundant peaks	Pure compound (% inten- sities)	Test spectra (% intensities)	
LC4a and LC4b					
				LC4a	LC4b
Naphthalene	128	128	100	14	36
		127	12	6	7
		129	11	2	5
		64	7	2	4
		51	7	11	17
		126	6	4	9
		102	6	5	8
		63	4	12	26
Anthracene	178	178	100	100	100
		176	17	20	54
		179	16	22	62
		89	14	23	43
		76	11	20	47
		88	9	13	31
		151	6	11	27
		152	6	14	36
Phenanthrene	178	178	100	100	100
		179	15	22	62
		176	15	20	54
		89	14	23	43
		76	14	20	47
		88	11	13	31
		177	8	9	27
		152	6	14	36
9-Methylanthracene	192	Not given			
9-Methyl phenan- threne	192	192	100	80	37
		191	39	80	23
		189	16	27	9
		193	15	14	6
		94.5	12	11	4
		82.5	11	9	4
		96	11	6	3
		165	8	16	5
9,10-Dimethyl anthracene	206	Not given			

(continued)

TABLE 24. (continued)

	MW	Eight most abundant peaks	Pure compound (% inten- sities)	Test spectra (% intensities)	
9,10-Dimethyl phenanthrene	206	206	100	100	14
		191	84	80	23
		207	17	21	3
		189	15	27	9
		89	15	23	43
		192	13	80	37
		101	12	7	6
		82.5	11	9	4
2,3-Dimethyl naphthalene	156	156	100		21
		141	70		17
		155	24		7
		157	14		3
		115	13		8
		76	10		47
		153	9		6
		128	8		36
LC5a Fluorene	166	166	100	65	
		165	80	33	
		82.5	15	8	
		167	15	82	
		163	12	5	
		83	11	5	
		164	10	12	
		82	8	5	
2,3-Benzofluorene	216	216	100	13	
		215	78	10	
		217	18	2	
		107.5	16	3	
		213	15	2	
		108	13	3	
		106.5	8	1	
		94.5	7	2	
n-Ethylcarbazole	195	180	100	100	
		195	42	100	
		152	17	34	
		166	13	65	
		140	10	25	
		139	8	27	
		151	8	34	
		196	8	18	

(continued)

TABLE 24. (continued)

	MW	Eight most abundant peaks	Pure compound (% inten- sities)	Test spectra (% intensities)
2-Methyl indole	131	130 131 77 103 65	100 85 19 15 10	34 23 12 3 5
Carbazole	167	167 166 139 168 140 83.5 70.5 63	100 26 17 16 11 9 5 4	82 65 27 10 25 4 1 23
2,3-Dimethyl indole	145	144 145 130 143 77 146 43 30	100 89 35 17 11 10 10 9	12 12 34 3 12 1 2 Not recorded
LC5b				
7,8-Benzoquinoline	179	179 178 180 89.5 151 76 89 152	100 21 14 11 9 8 8 8	100 20 100 9 11 19 5 13
Phenanthradine	179		Not given	
1,10-Phenanthroline	180	180 179 154 153 181 90 152 127	100 31 18 16 14 10 9 9	100 100 5 11 16 15 13 4

(continued)

TABLE 24. (continued)

	MW	Eight most abundant peaks	Pure compound (% inten- sities)	Test spectra (% intensities)
Phenazine	180	180 179 90 76 153 128 63 154	100 20 12 12 7 6 6 5	100 100 15 19 11 2 12 5
Anthrone	194	194 165 166 195 63 82.5 163 82	100 88 17 15 15 14 12 12	7 9 2 2 12 2 2 1
LC6a				
2-Hydroxy pyridine	95	95 67 39 41 40 38 66 96	100 35 27 13 11 11 10 9	100 98 Not recorded 20 Not recorded Not recorded 11 6
				LC6a LC6b
2,6-Dimethyl phenol	122	122 107 121 77 39 91 51 79	100 83 38 32 30 23 20 19	7 6 3 7 Not recorded 3 18 2 Not recorded Not recorded 1 11 3
6-6-Biphenol	186	186 157 158 131 187 139 128 185	100 28 23 22 13 12 11 11	21 10 7 11 3 8 8 2

(continued)

TABLE 24. (continued)

	MW	Eight most abundant peaks	Pure compound (% inten- sities)	Test spectra (% intensities)
LC6b				
9-Fluorenone	180	180	100	15
		152	26	18
		76	16	9
		181	14	5
		151	13	25
		150	7	20
		63	7	10
		75	5	19
o-Phenoxybenzoic acid	214	121	100	10
		214	31	5
		51	20	11
		77	14	6
		39	13	Not recorded
		65	12	3
		120	10	3
		122	8	3
1-Fluorene carboxylic acid	210	Not listed		
9-Fluorenone-4- carboxylic acid	224	224	100	100
		225	18	12
		207	18	20
		151	18	25
		179	17	20
		152	9	18
		139	8	22

4.3.2 Verification of Mixtures

It was not necessary to verify the mixtures prior to shipment to the contractors because the objective of this round of analyses was to test the contractors' generation and interpretation of spectra for the presence of the mixture compounds. Their reported LRMS and IR spectra were verified by comparison to Eight Peak Index and Sadtler Reference spectra as in Section 4.2. The LRMS verification data for the pure compounds are given in Table 25.

4.4 GENERATION AND VERIFICATION OF TAR SAMPLE

4.4.1 Generation of Tar Sample

A coal gasification tar sample, #52 (RTI), was collected from a model gasifier, dissolved in methylene chloride, packaged in sealed vials, and sent to the contractors.

4.4.2 Verification of Tar Sample

RTI capillary column GC data on this tar sample are given in Table 26. An outside laboratory also performed high-resolution mass spectrometric analyses of the unfractionated tar sample. Data from these analyses are given in Table 27. Thirteen masses representing 26 of the 30 compounds searched for by this laboratory were detected.

4.5 INSTRUCTIONS TO THE CONTRACTORS

4.5.1 Test Spectra

Copies of the IR and LRMS spectra sent to the contractors are shown in Figures 1 through 12. The IR spectra actually sent to the contractors were 16 x 5 inches, or two-thirds normal size. The contractors were to interpret the IR and LRMS test spectra as they would normally interpret actual Level 1 spectra. A copy of the organic analysis chapter of the Level 1 Environmental Assessment Manual, (Second edition, Lentzen et al.) was provided for guidance in completing this task. No special efforts were to be made with the interpretation beyond those expected for Level 1 work. For the purpose of this study, though, it was extremely important that the spectral characteristics leading to the identification of functional groups, structural characteristics, or, when possible, individual compounds or categories of compounds be clearly identified. To accomplish this, two types of reporting forms were provided for both the IR and LRMS test spectra. One type was the Level 1 reporting

TABLE 25. LOW RESOLUTION MASS SPECTRAL VERIFICATION
DATA FOR COMPOUNDS IN SYNTHETIC TEST MIXTURES

Compound	MW	Eight most abundant peaks	Pure compound (% intensities)
LC5 Fluorene			
2,3-Benzofluorene			
7,8-Benzoquinoline			
1,10-Phenanthroline		See Table 23	
Phenazine			
Anthrone			
2,6-Dimethyl quinoline	157	157 156 158 115 142 39 51 63	100 33 13 10 9 8 7 7
LC6 9-Fluorenone		See Table 23	
1-Fluorene carboxylic acid		See Table 23	
9-Fluorenone-4-carboxylic acid		See Table 23	
2-Methyl-1-tetralone	160	118 160 90 145 131 119 91 39	100 72 38 21 17 10 10 10
2-Tert-butylphenol	150	135 107 150 91 115 136 41 77	100 67 37 14 13 10 8 7
2-Methyl-1,4-naphthoquinone	172*	104 144 76 115 116 50 105 75	100 90 80 68 67 35 27 25

*Although the Eight Peak Index gives the intensity of molecular ion 172 as 0.00, this is incorrect. Ion 172 should be significant.

TABLE 26. VERIFICATION DATA FOR COAL GASIFICATION TAR SAMPLE
ANALYZED BY DIRECT CAPILLARY GC/MS

Category	Compounds	Expected LC fraction	Weight of tar (%)
Fused alternate, nonalternate hydrocarbons	Naphthalene	2,3	0.6
	2-Methyl naphthalene	2,3	0.4
	1-Methyl naphthalene	2,3	0.3
	C ₂ =naphthalenes	2,3	0.5
	Biphenyl	2,3	0.2
	Acenaphthylene	2,3	0.7
	Acenaphthene	2,3	0.3
	Fluorene	2,3	0.6
	Phenanthrene	2,3	1.6
	Anthracene	2,3	0.6
	Fluoranthene	2,3	0.5
	Pyrene	2,3	0.4
	Benzo(a)fluorene	2,3	0.2
	Benzo(b)fluorene	2,3	0.1
	Benzo(a)anthracene	2,3	0.3
	Chrysene + triphenylene	2,3	0.3
	Benzo(b)fluoranthene	2,3	0.1
	Benzo(e)pyrene	2,3	0.1
	Benzo(a)pyrene	2,3	0.1
	Perylene	2,3	0.03
	Dibenzo(a,h)anthracene	2,3	0.1
	Indeno(1,2,3-cd)pyrene	2,3	NG
	Benzo(g,h,i)perylene	2,3	0.05
Heterocyclic sulfur compounds	Benzothiophene	4	0.2
Heterocyclic oxygen compounds	Dibenzofuran	3,4	0.6
Heterocyclic nitrogen compounds	Carbazole	4	0.2
	Benzidine	6	0.1
	Alkyl pyridines	6	NG
	Quinoline	6	NG
	Alkylquinolines	6	NG
	Alkyl benzoquinolines	6	NG
	Acridine	6	NG
Phenols	Phenol	6	NG
	Cresols	6	NG
	Xylenols	6	NG
	o-Isopropylphenol	6	NG
	Trimethyl phenol	6	NG

NG = Not given.

TABLE 27. HIGH-RESOLUTION MASS SPECTRAL ANALYSIS OF UNFRACTIONATED COAL GASIFICATION TAR SAMPLE

Mass		Δ MMU	Percent relative intensity	Formula			Compounds
Precise	Measured			C	H	N	
166.0783	166.0763	2	2.3	13	10		Fluorene
178.0783	178.0777	1	9.1	14	10		Anthracene Phenanthrene
179.0735	179.0803	7	1.2*	13	9	1	Acridine
202.0783	202.0754	3	10.4	16	10		Pyrene Fluoranthene
216.0939	216.0930	1	2.7	17	12		Benzo(a)fluorene Benzo(b)fluorene
228.0939	228.0948	1	4.3	18	12		Chrysene Triphenylene Benzo(a)anthracene Benzo(c)phenanthrene
252.0939	252.0907	3	4.0	20	12		Benzo(b)fluoranthene Benzo(j)fluoranthene Benzo(k)fluoranthene Benzo(a)pyrene Benzo(e)pyrene Perylene
254.1095	254.1024	7	0.6	20	14		Cholanthrene [Benz(j)- aceanthrylene]
256.1252	256.1158	9	0.4	20	16		7,12-Dimethylbenz(a)- anthracene
268.1252	268.1073	18	0.3	21	16		3-Methylcholanthrene
276.0939	276.0937	0	0.9	22	12		Benzo(ghi)perylene
278.1095	278.1053	4	0.5	22	14		Dibenz(a,b)anthracene
302.1095	302.1084	1	0.1	24	14		Dibenzo(a,b)pyrene Dibenzo(a,i)pyrene Dibenzo(b,def)chrysene

*Corrected for C¹³ contribution from mass 178.

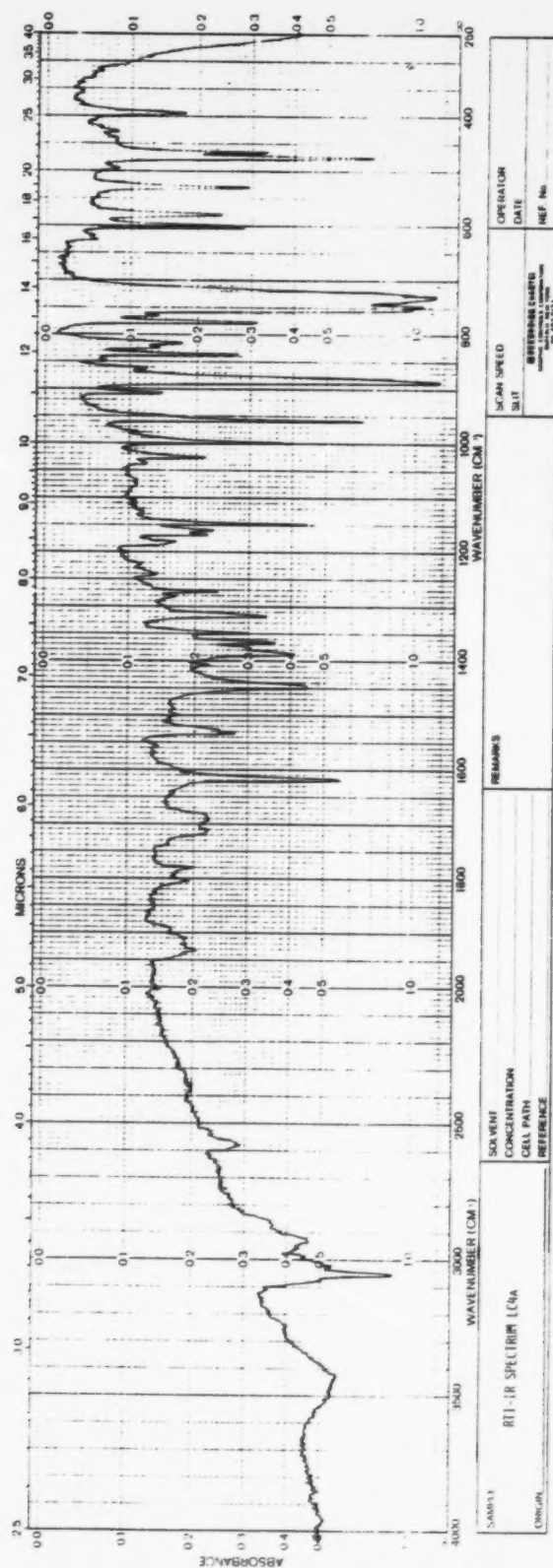


Figure 1. RTI IR spectrum LC4a.

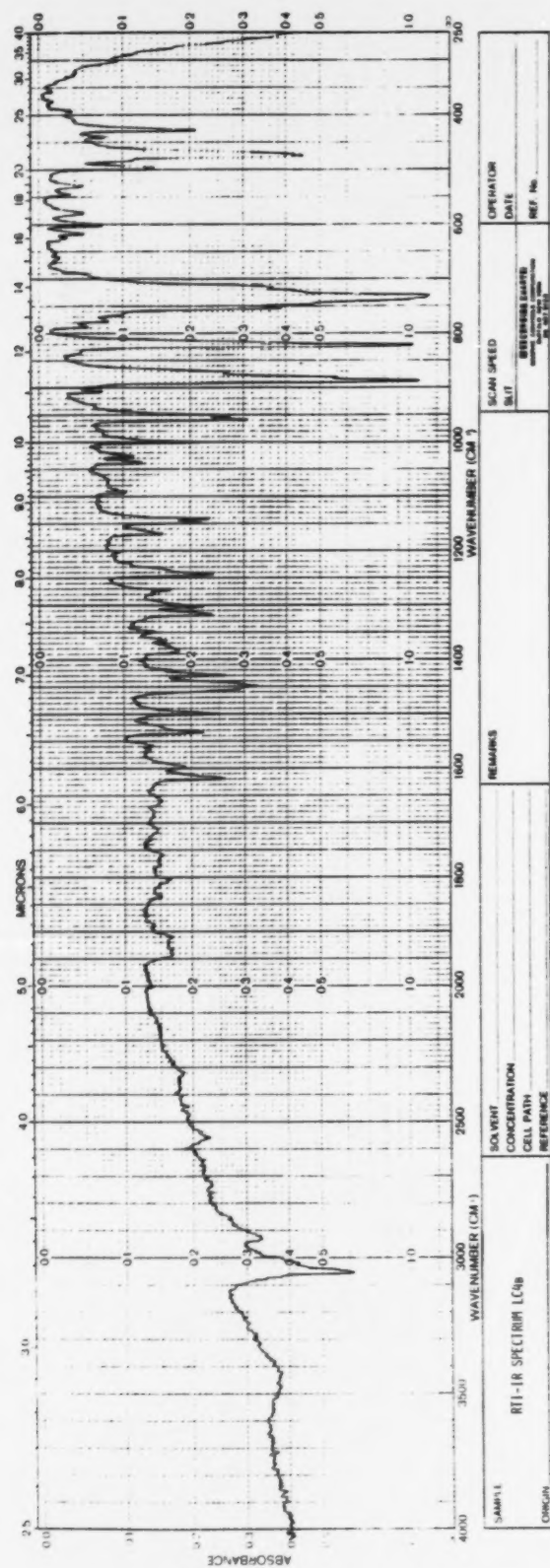


Figure 2. RTI IR spectrum LC4b.

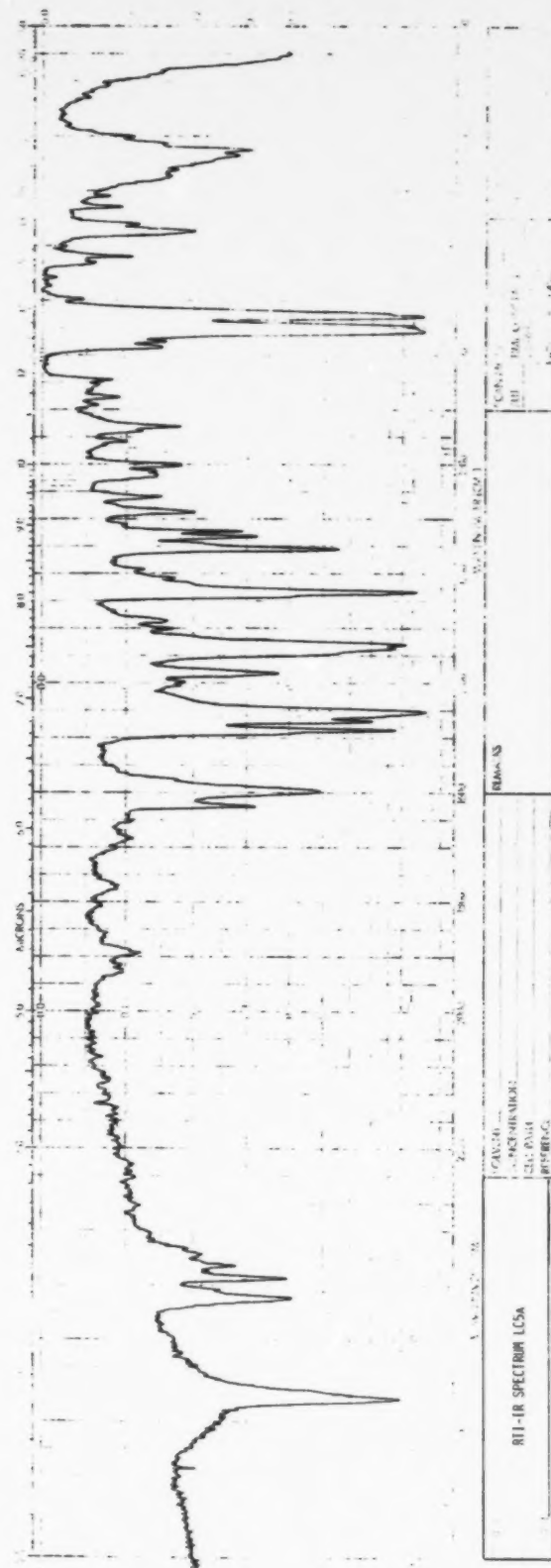


Figure 3. RTI IR spectrum LC5a.

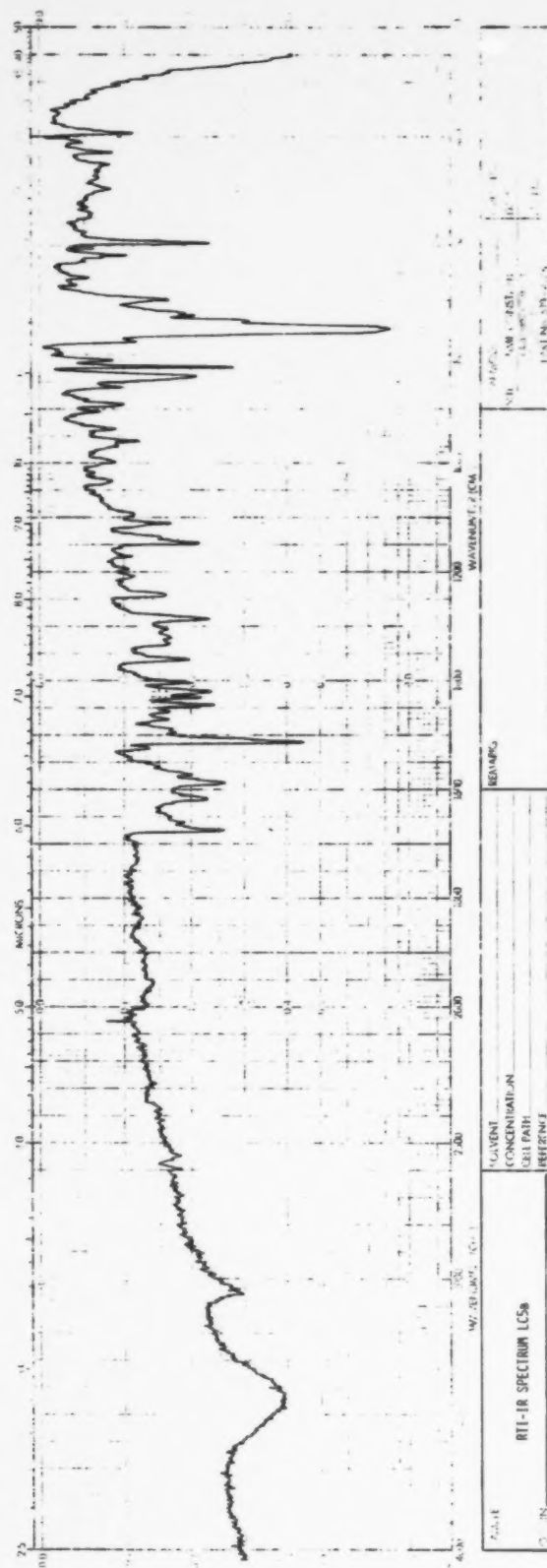


Figure 4. RTI IR spectrum LC5b.

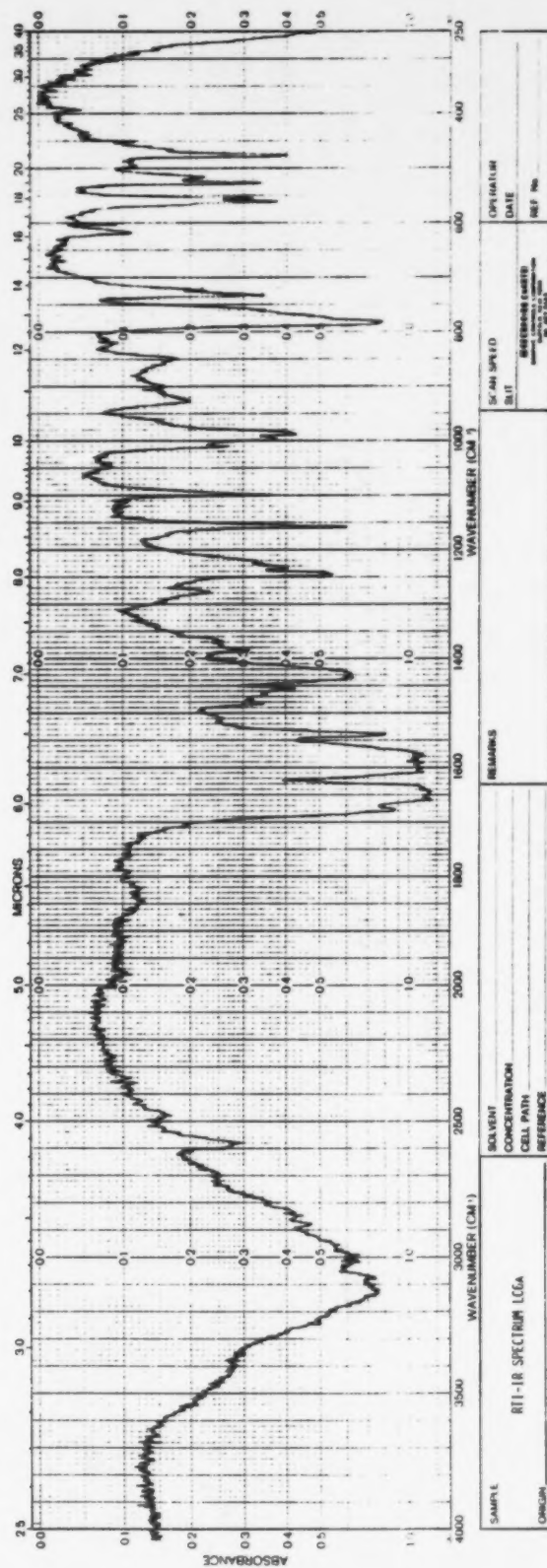


Figure 5. RTI IR spectrum LC6a.

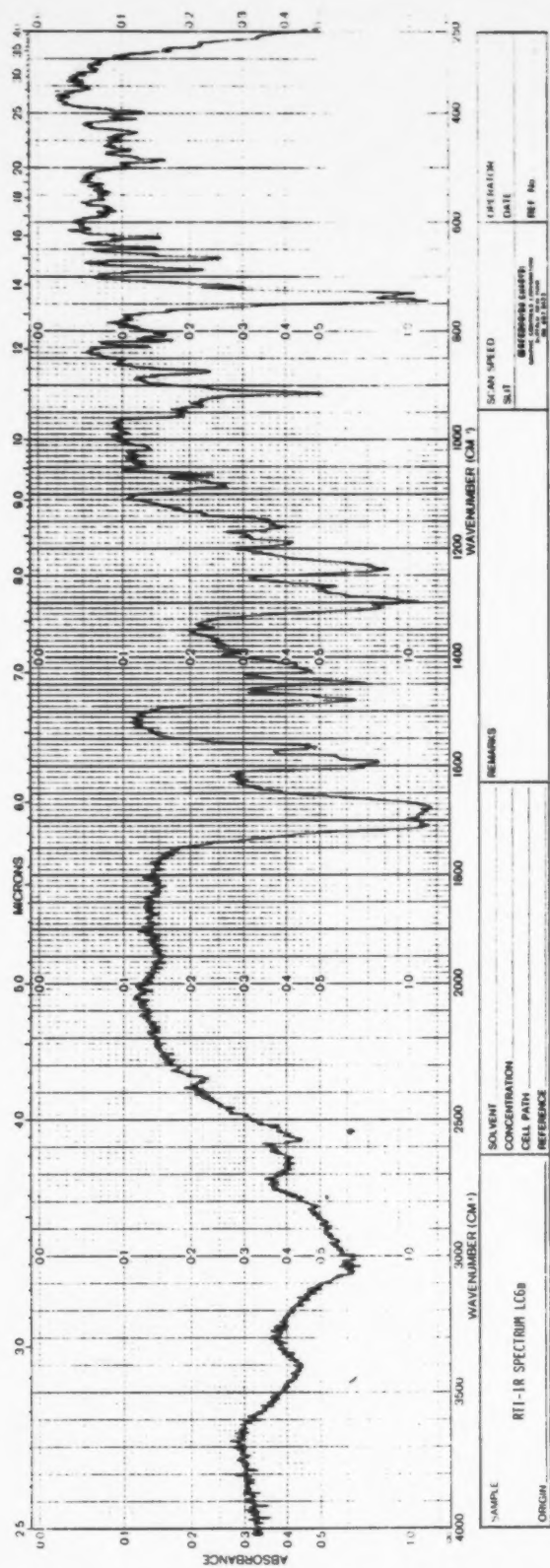


Figure 6. RTI IR spectrum LC6b.

800400. 13 16-MAR-78

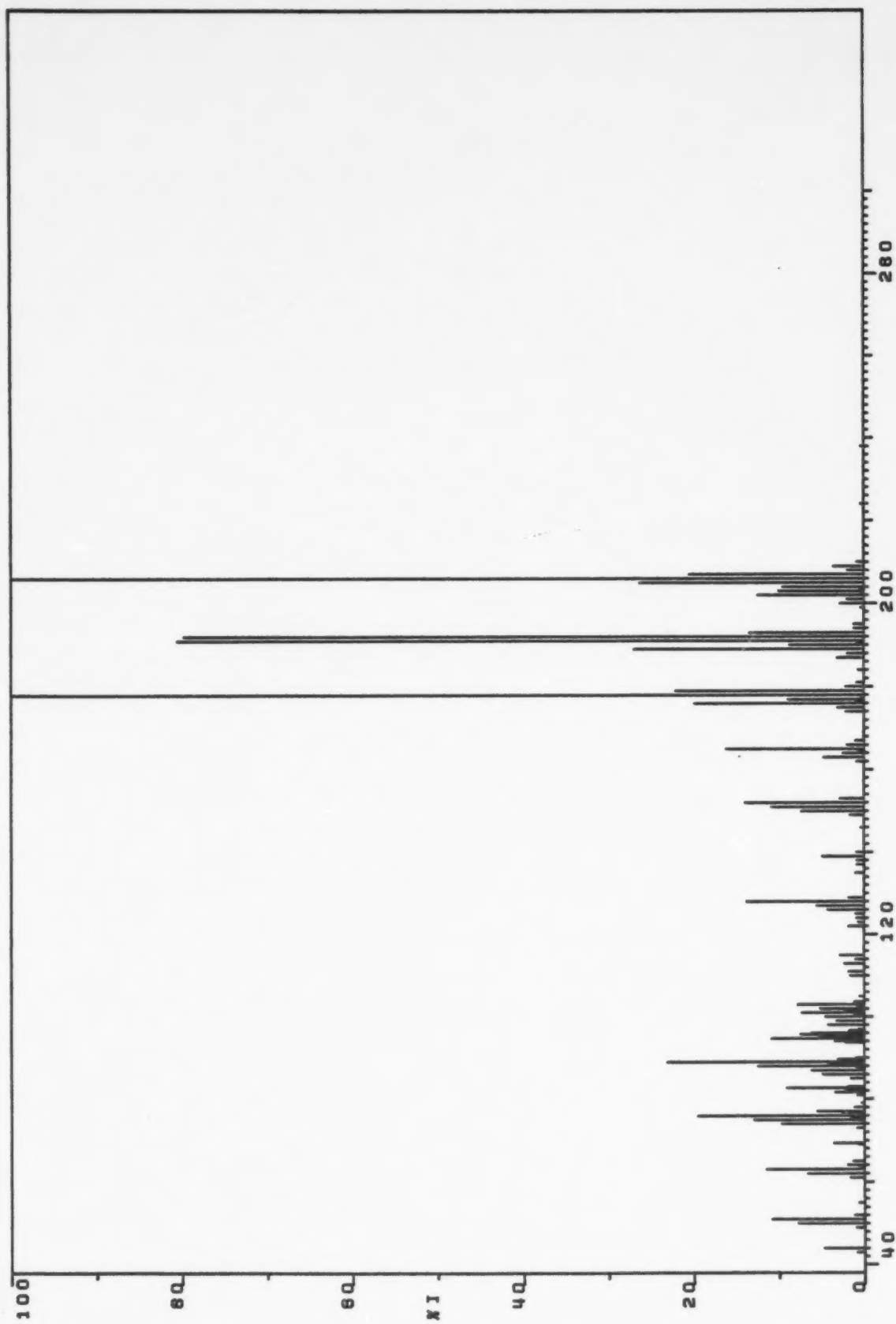


Figure 7. RTI LRMS spectrum LC4a.

AB0500. 32 18-MAR-78

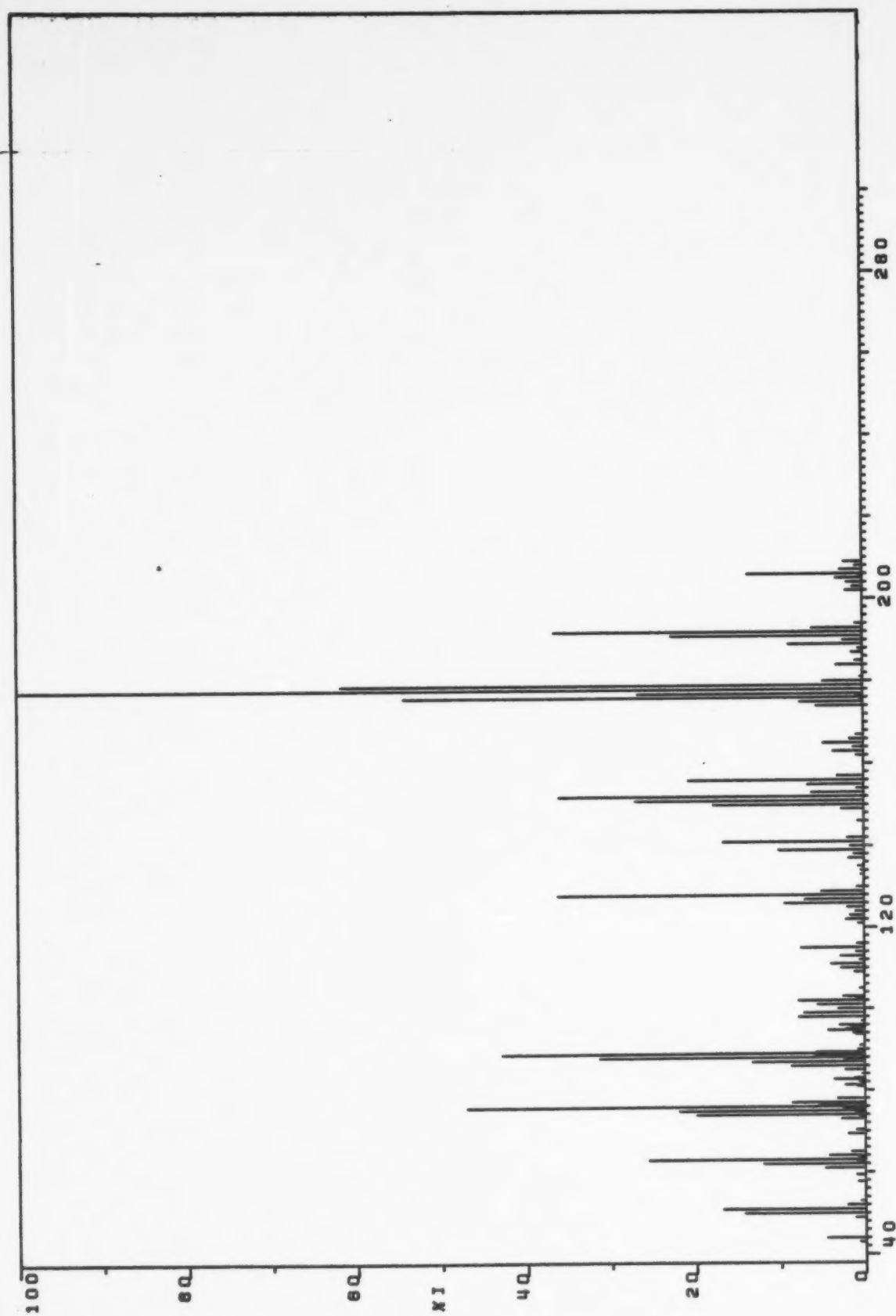


Figure 8. RTI LRMS spectrum LC4b.

AG0100. 9 16-MAR-79

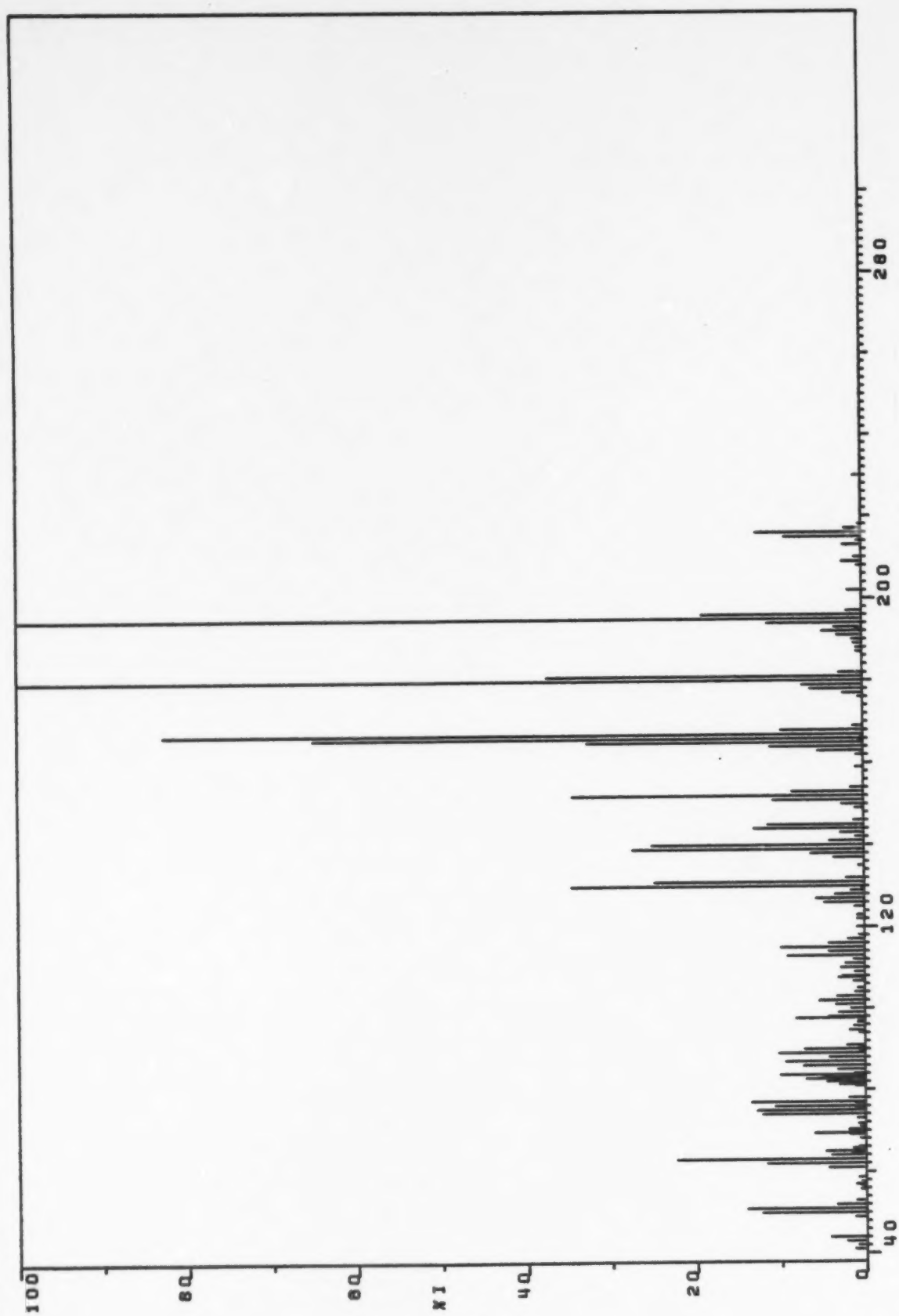


Figure 9. RTI LRMS spectrum LC5a.

AS0200. 9 16-MAR-79

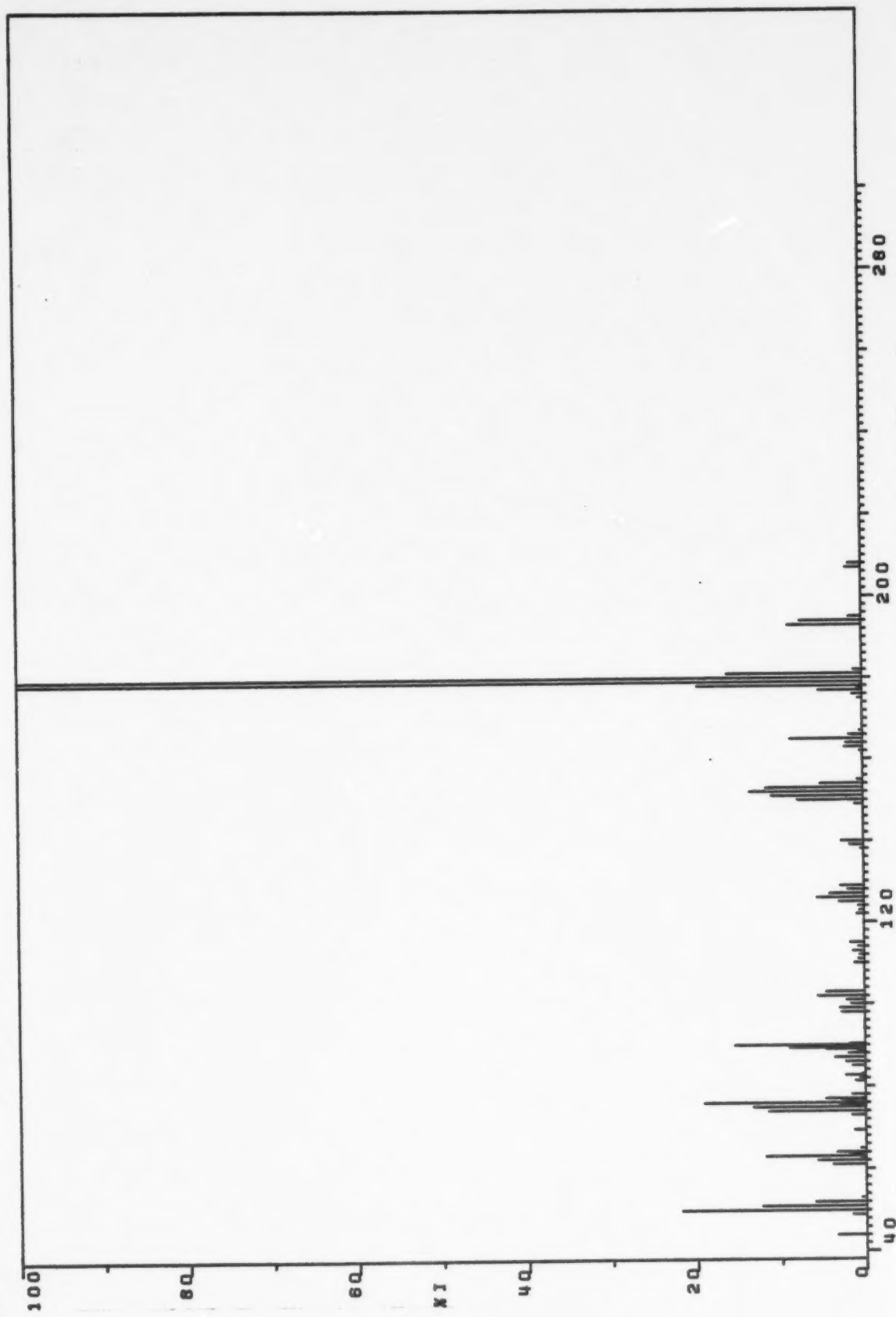


Figure 10. RTI LRMS spectrum LC5b.

80300. 4 18-MAR-79

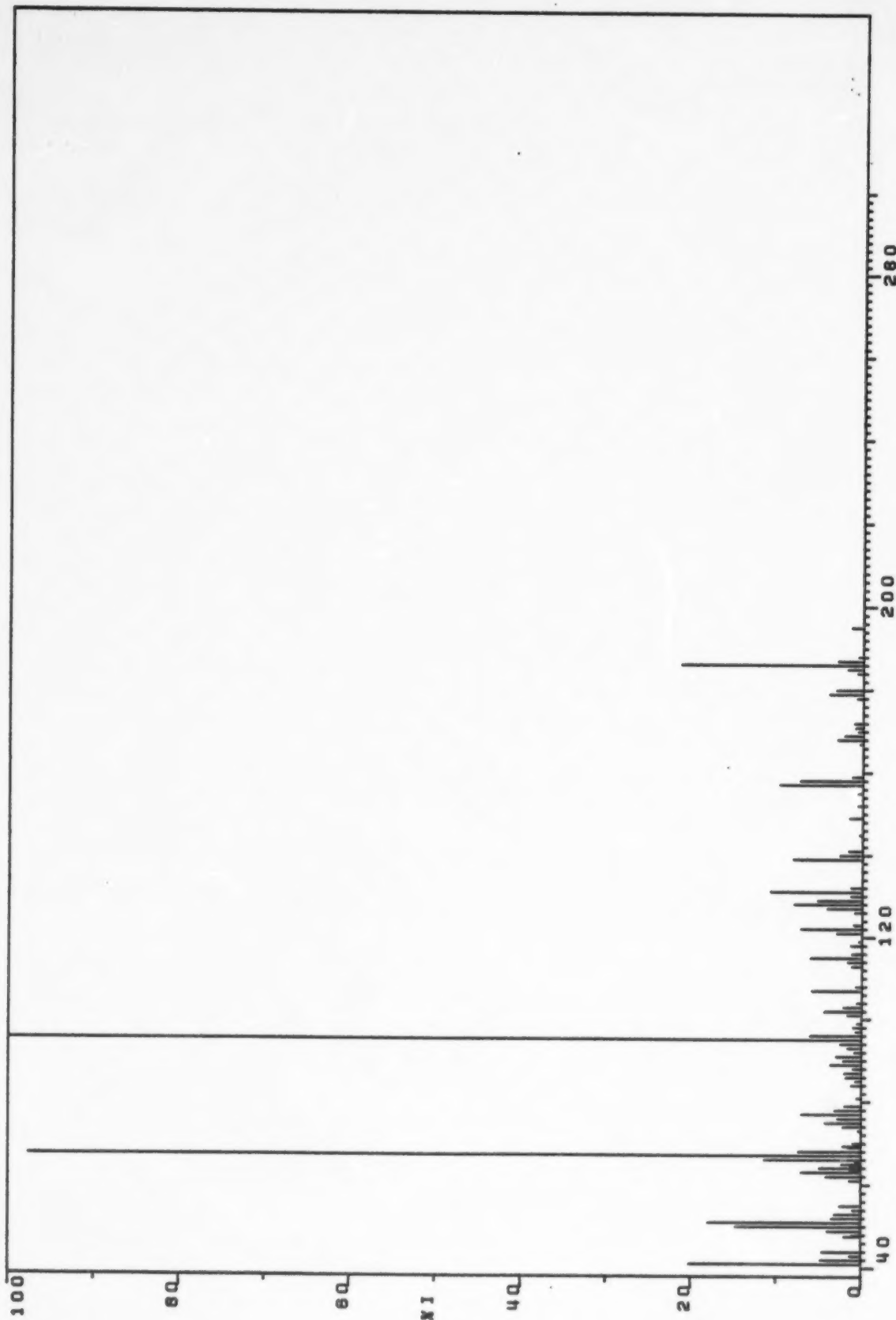


Figure 11. RTI LRMS spectrum LC6a.

AB0100. 22 16-MAR-78

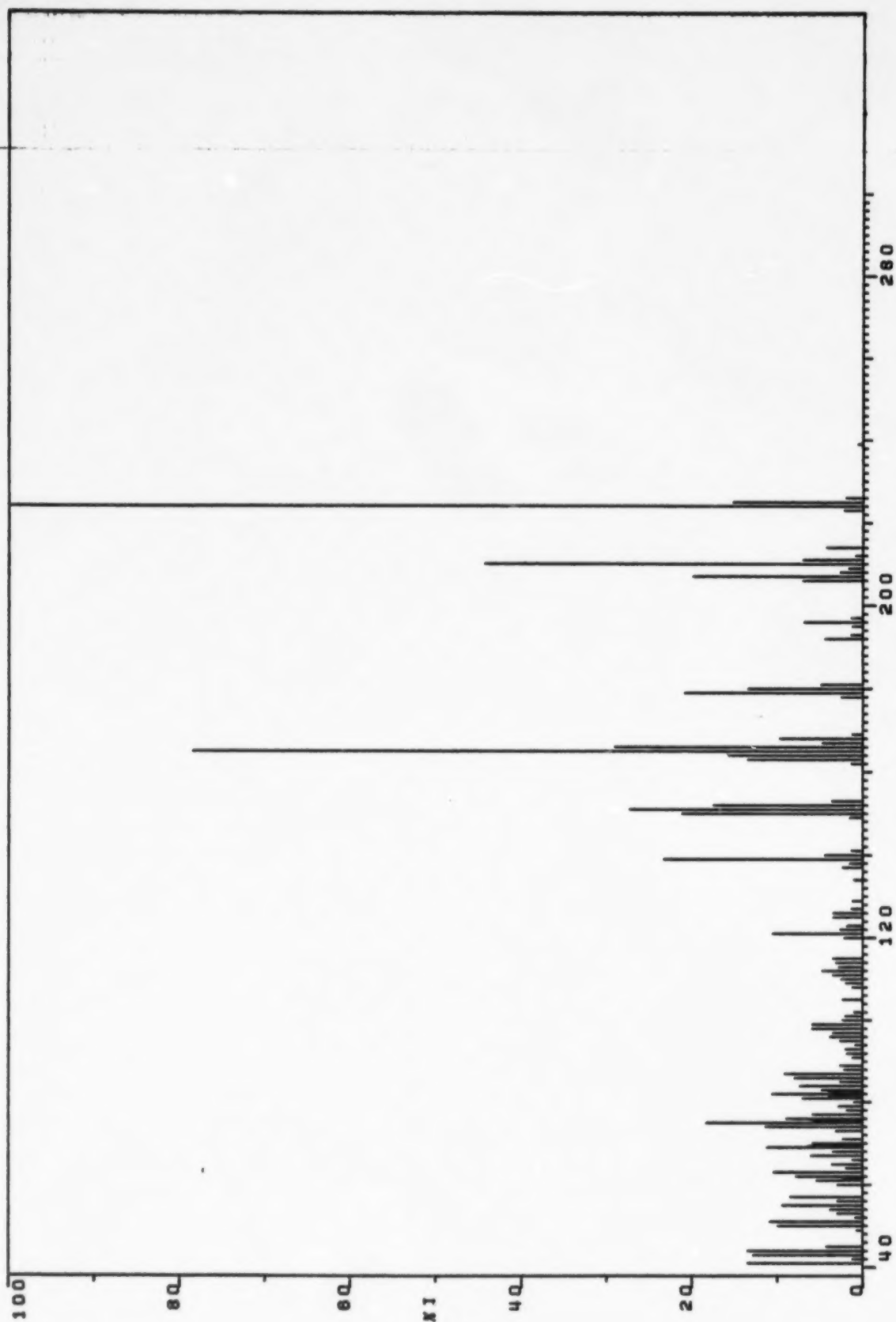


Figure 12. RTI LRMS spectrum LC6b.

forms as called for in the Level 1 manual (Figures 13 and 14). The other type of form was specially prepared for this study (Figures 15 and 16) to assist the analyst in spelling out the reasoning behind each assignment. These latter forms requested information about the type of signal characterized (whether one peak or a pattern of peaks); the signal assignment as a structural moiety, functional group, compound, or class of compounds; and, finally, the assignment rationale, a discussion and/or listing of the data inputs that lead to the assignment of compound/category in the Level 1 reporting forms. This discussion might include information about peak wavelength or mass, peak magnitude or shape, and patterns of peaks or correlation with the LC fraction number. Also, the forms asked for an explanation of whether or not the LRMS data proved useful to the IR interpretation.

4.5.2 Test Mixtures

The synthetic mixtures LC5 and LC6, the tar sample, and the respective solvent blanks were to be analyzed as normal Level 1 samples using the instrumentation and conditions normally used to analyze Level 1 samples. The reporting forms and instructions for completing these forms were identical to those discussed in Section 4.5.1. In addition, the contractors were to send RTI copies of the IR and LRMS spectra they generated.

IR ANALYSIS REPORT

Contractor _____

Sample Site _____ Sample Acquisition Date _____

Type of Source _____

Test Number _____ Sample ID Number _____

Sample Description _____

Analyst Responsible _____ Date Analyzed _____ Time _____

Calculations and Report Reviewed By _____ Report Date _____

Instrument _____ Sample Cell Type _____

Utilized Max/Min Signal Intensity Values _____

Observations _____

Figure 13. Level 1 IR analysis report form.

SAMPLE: _____

[illegible]

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LRMS ANALYSIS REPORT

Contractor _____

Sample Site _____ Sample Acquisition Date _____

Type of Source _____

Test Number _____ Sample ID Number _____

Sample Description _____

Analyst Responsible _____ Date Analyzed _____ Time _____

Calculations and Report Reviewed By _____ Report Date _____

Instrument _____

Resolution _____

Sample Size _____ Batch Inlet _____ Probe Inlet _____

Observations _____

Figure 14. Level 1 LRMS analysis report form.

LRMS REPORT

SAMPLE: _____

Major Categories

Intensity	Category	MW Range

Sub-Categories, Specific Compounds

Intensity	Category	m/e	Composition

Other

Figure 14. (continued)

IR ANALYSIS

CONTRACTOR _____ DATE _____

IR SPECTRUM NUMBER _____

ANALYST(S) _____

TYPE OF SIGNAL CHARACTERIZED: PEAK _____ OR PATTERN OF PEAKS _____

SIGNAL WAVENUMBER VALUE(S) OR RANGE _____

SIGNAL ASSIGNMENT(S)*: _____

ASSIGNMENT RATIONALE (SIGNAL WAVENUMBER, SIGNAL SHAPE OR MAGNITUDE,
LC FRACTION, RELATION TO OTHER IR SIGNALS, RELATION TO LRMS DATA,
ETC.) _____

*Assign as structural moieties, functional groups, compounds, or
classes of compounds in decreasing order of likelihood.

Figure 15. IR analysis report form.

LRMS ANALYSIS

CONTRACTOR _____ DATE _____

LRMS SPECTRUM NUMBER _____

ANALYST(S) _____

NATURE OF SIGNAL CHARACTERIZED: PEAK ____ OR PATTERN OF PEAKS ____

SIGNAL m/e VALUE(S) _____

SIGNAL ASSIGNMENT(S)*: _____

ASSIGNMENT RATIONALE (SIGNAL MASS, SIGNAL MAGNITUDE, LC FRACTION,
ISOTOPE ABUNDANCES, RELATION TO OTHER MS SIGNALS, RELATION TO IR
DATA, ETC.) _____

* Assign structural moieties, functional groups, compounds, or classes
of compounds in decreasing order of likelihood.

Figure 16. LRMS analysis report form.

SECTION 5

RESULTS OF IR MEASUREMENT AND INTERPRETATION

5.1 INTERPRETATION OF TEST IR SPECTRA

5.1.1 Introduction

In this first phase of the study, six spectra were prepared and sent to four contractors for interpretation. Included were two different spectra representing each of the LC fractions 4, 5, and 6; one of each set was prepared so that it was more difficult to interpret than the other. The results of the contractors' interpretations are presented in Appendix B, Tables B-1 through B-6, and the RTI evaluation of these interpretations is presented below. Points considered in making this evaluation included assignment errors, alternate but acceptable assignments, assignment biases, and omissions.

5.1.2 Contractor A

5.1.2.1 Spectrum LC4a--

The sample from which spectrum LC4a was prepared contained polycyclic compounds, such as naphthalene and phenanthrene, and methyl derivatives of some of these compounds.

"A" correctly identified the presence of aromatic rings (1620 cm^{-1} , 1530 cm^{-1} , 1450 cm^{-1}), unsaturated CH (3060 cm^{-1}), and saturated CH (2930 cm^{-1} , 2850 cm^{-1}). Other aromatic bands below 1200 cm^{-1} were also correctly assigned.

"A" described a weak $3600\text{--}3300\text{ cm}^{-1}$ band as being due to OH or NH stretch. It most likely resulted from H_2O in the KBr pellet used. Bands at 1805 cm^{-1} , 1715 cm^{-1} , and 1690 cm^{-1} were described as being due to C=O. The latter two could possibly result from C=O contamination, though they all most likely are summation bands. A band at 1450 cm^{-1} was described as being due to aromatic or heteroaromatic ring stretching. It could also be due, in part, to CH_3 , as could the 1380 cm^{-1} band, which was not assigned.

5.1.2.2 Spectrum LC4b--

The sample from which spectrum LC4b was prepared contained the same type of compounds used to prepare LC4a.

"A" correctly identified the presence of aromatic rings (1620 cm^{-1} , 1530 cm^{-1} , 1450 cm^{-1} , and bands below 1000 cm^{-1}), unsaturated CH (3050 cm^{-1} , signals below 1000 cm^{-1}), and saturated CH (2930 cm^{-1}).

Aromatic overtone and summation bands in the $2000\text{--}1650\text{ cm}^{-1}$ range were not interpreted. Also CH_3 , which is indicated by bands at 1450 cm^{-1} , 1383 cm^{-1} , and 1364 cm^{-1} , was not identified.

5.1.2.3 Spectrum LC5a--

The sample from which spectrum LC5a was prepared contained aromatic and methylene groups (fluorene), secondary and tertiary amine groups (carbazole and indole), and methyl and ethyl derivatives of the carbazole and indole compounds.

"A" correctly identified the presence of NH (3410 cm^{-1} , 1630 cm^{-1}), unsaturated CH (3050 cm^{-1}), saturated CH (2970 cm^{-1} , 2930 cm^{-1}), CH_3 (1450 cm^{-1}), and aromatic rings (1485 cm^{-1} , 1450 cm^{-1} , and bands below 1000 cm^{-1}).

Signals at 1650 cm^{-1} and 1680 cm^{-1} were described as being due to C=O ; they are probably overtone or summation signals. A band at 1235 cm^{-1} was described as being due to C-O of aromatic alcohol or ether. This assignment is not unreasonable although the band is probably due to C-N stretch in the carbazoles. Also, alcohols are not indicated by other bands in the spectrum.

5.1.2.4 Spectrum LC5b--

The sample from which spectrum LC5b was prepared contained aromatic and heteroaromatic structures (7,8-benzoquinoline, phenazine) and methylene and carbonyl structures (anthrone).

"A" correctly identified the presence of aromatic and heteroaromatic rings (1585 cm^{-1} , 1515 cm^{-1} , 1445 cm^{-1} , and bands below 1000 cm^{-1}) and the C=O of the quinone group (1675 cm^{-1}).

"A" described a signal in the $3600\text{--}3300\text{ cm}^{-1}$ range as being due to OH or NH; it probably is due to H_2O in the KBr. A band at 1620 cm^{-1} was described as being due to the NH bend of a primary or secondary amine. The wave number is high for a secondary amine; the signal could be partly the result of an aromatic stretch. Bands at 1280 cm^{-1} and 1240 cm^{-1} were de-

scribed as being due to aromatic ether or alcohol; they are probably due, in part, to C-C-C bending and C-C stretching of $=C(CO)-C=$, i.e., anthrone.

5.1.2.5 Spectrum LC6a--

The sample from which spectrum LC6a was prepared contained aromatic, phenol, and methyl structures (2,6-dimethyl phenol and o-6-biphenol) and a nitrogen-containing heterocycle as well as an amine structure (2-hydroxypyridine-pyridone in tautomeric equilibrium).

"A" correctly identified the presence of OH or NH structures ($3600-3350\text{ cm}^{-1}$), OH structures ($3350-2400\text{ cm}^{-1}$), carbonyl structures (1650 cm^{-1}), C-O stretch of aromatic alcohols (1240 cm^{-1}), and aromatic and heteroaromatic structures (1600 cm^{-1} , 1580 cm^{-1} , 1540 cm^{-1} , and bands below 1000 cm^{-1}).

"A" assigned a band at 1680 cm^{-1} as strong. This band was a shoulder on a much stronger band at 1650 cm^{-1} , which was, in fact, at near-infinite absorbance. If the spectrum had been optimized, it is likely that the band at 1680 would have been weak or medium, making assignment as a summation or overtone band more likely. A strong band at 1160 cm^{-1} , which was not assigned, is probably due to C-O of aromatic alcohols or C-N structure. Another strong band at 1100 cm^{-1} , also not assigned, is probably due to C-O structure.

5.1.2.6 Spectrum LC6b--

The sample from which spectrum LC6b was prepared contained aromatic and ketone structures (fluorenone), carboxylic acid structures (carboxylic acid derivatives of fluorene and fluorenone), ether structures (o-phenoxybenzoic acid), and methyl and phenol structures (2,6-dimethyl-phenol).

"A" correctly identified OH structures ($3600-3300\text{ cm}^{-1}$, $3300-2400\text{ cm}^{-1}$), C=O of ketones (1680 cm^{-1}), and aromatic structures (1600 cm^{-1} , 1560 cm^{-1} , 1480 cm^{-1} , 1450 cm^{-1}).

"A" described the band at 1710 cm^{-1} as being due to the C=O of an acid, aldehyde, ketone, or conjugated or aromatic ester. These assignments are all reasonable, although from reference spectra of the mixture components, it appears that the band is due principally to a ketone.

"A" described 1240 cm^{-1} as being due to C-O of an aromatic ester, alcohol, or ether. An ester does not seem likely due to lack of a significant band at about 1735 cm^{-1} . The wavenumber appears to be somewhat high for an alcohol, though a band at this position is found in the reference spectrum of 2,6-dimethyl phenol. An antisymmetric C-O-C stretch of an ether at:

1240 cm^{-1} is reasonable; such an assignment agrees with what is present in the mixture and also is supported by a weak band at 1015 cm^{-1} , which could be the symmetric C-O-C stretch of an ether. The 1240 cm^{-1} band could also be due in part to the coupling of the OH bend and C-O stretch of a carboxylic acid dimer. A medium band at 915 cm^{-1} supports this latter assignment in that the 915 cm^{-1} band could be a result of OH out-of-plane bending of the acid dimer. "A" described a band at 1430 cm^{-1} as being due to CH_2 near S, P, Si, or C=O, or heteroaromatic ring stretching. This band could also be due to coupling between in-plane OH bending and C-O stretching of an acid dimer.

"A" assigned a strong band at 1300 cm^{-1} as being due to an aryl amine. This assignment is not out of line with other NH indicators (bands in the 3600-3300 cm^{-1} range, 1600 cm^{-1} , 1560 cm^{-1} , and bands in the 900-650 cm^{-1} range). The strong bands at 1710 cm^{-1} and 1680 cm^{-1} point, however, to the 1300 cm^{-1} band resulting from coupling between in-plane OH bending and C-O stretching of a carboxylic acid dimer.

5.1.3 Contractor B

"B" chose not to use the forms sent with the spectra. Instead, their interpretation results were presented in a table and in summary paragraphs. Not using the forms has made it difficult to evaluate the thoroughness of these spectral interpretations. "B" did, however, have three analysts, with 20 years, 3 years, and $\frac{1}{2}$ year of experience, interpret the spectra to emphasize the importance of experience. The most experienced spectroscopist was somewhat more successful than the other two in making correct assignments. The second and third spectroscopists made about the same number of correct assignments though the second-most-experienced spectroscopist made the largest number of incorrect assignments. Finally none of "B's" spectroscopists did as well as the other contractors' spectroscopists, apparently because they did not interpret many of the spectral bands.

5.1.3.1 Spectrum LC4a--

The most experienced spectroscopist at "B" correctly identified the presence of fused-ring aromatics (750-700 cm^{-1}). This analyst apparently did not interpret the bands at 2930 cm^{-1} , 2850 cm^{-1} , and 1380 cm^{-1} that collectively indicate the presence of CH_3 groups.

5.1.3.2 Spectrum LC4b--

"B" correctly identified the presence of fused-ring aromatics. The principal analyst did not indicate the presence of alkyl substitution, though the other two analysts did.

5.1.3.3 Spectrum LC5a--

"B" correctly identified the presence of NH (3420 cm^{-1}), heterocyclic and aromatic fused ring ($800\text{--}700\text{ cm}^{-1}$), and saturated CH ($3000\text{--}2900\text{ cm}^{-1}$) structures. "B" stated that the intensity of the OH/NH band indicates that the oxygen or nitrogen is in the ring system. The second-most-experienced analyst indicated the presence of an ortho-substituted phenol and the least-experienced analyst indicated the presence of an aromatic amine, neither of which is unreasonable.

5.1.3.4 Spectrum LC5b--

"B" correctly identified the presence of aromatic ring (1600 cm^{-1}) and fused ring ($800\text{--}700\text{ cm}^{-1}$) structures. They did not indicate the presence of aliphatic substitution.

"B" did not interpret the 1675 cm^{-1} band, which is due to C=O of quinone. The second-most experienced analyst indicated the presence of aromatic sulfone and substituted naphthalene, both of which are incorrect. The least-experienced analyst indicated the presence of an aromatic nitrogen heterocycle, which is correct.

5.1.3.5 Spectrum LC6a--

"B" correctly identified the presence of OH and/or NH. "B" further stated that this latter identification coupled with strong bands at 1600 cm^{-1} and 1700 cm^{-1} indicated the presence of an amino acid; subsequently, 2-pyridinol was correctly identified.

The principal analyst did not indicate the presence of aromatic rings (1600 cm^{-1}) or aromatic alcohols (1245 cm^{-1} , 1160 cm^{-1} , 1100 cm^{-1}).

The second-most-experienced analyst indicated the presence of a carboxylic acid salt and aromatic amide. The least-experienced analyst also indicated aromatic amides, which is reasonable.

5.1.3.6 Spectrum LC6b--

"B" correctly identified the presence of carboxylic acids (broad OH band, 1680 cm^{-1} , 1420 cm^{-1} , 1270 cm^{-1} , 920 cm^{-1}), aromatic ring structures, and keto carbonyls (1710 cm^{-1}).

"B" did not indicate the presence of ethers (1240 cm^{-1} , 1015 cm^{-1}) or aromatic alcohols (1190 cm^{-1} , 1160 cm^{-1}). The second-most-experienced analyst correctly indicated the presence of ketone though incorrectly indicated the presence of fused aromatic rings and sulfuric acid salt. The least-experienced analyst correctly identified the presence of an ortho-substituted, aromatic carboxylic acid.

5.1.4 Contractor C

"C" interpreted essentially every band in each spectrum. Many of the major bands were interpreted as resulting from particular structural moieties and/or functional groups. The remainder, and subsequently the majority, of the bands were interpreted as resulting from particular compounds. Interpretation according to compound followed preliminary compound identification using both IR and LRMS, and was performed in order to verify compound identification.

5.1.4.1 Spectrum LC4a--

"C" correctly identified H_2O in KBr ($3650\text{--}3200\text{ cm}^{-1}$), unsaturated CH ($3100\text{--}3000\text{ cm}^{-1}$), saturated CH ($3000\text{--}2800\text{ cm}^{-1}$), aromatic rings (1618 cm^{-1} , 1532 cm^{-1}), and CH_3 (1376 cm^{-1}) structures.

The only comment that might be added is that the band at 1448 cm^{-1} , which was described as being due to aromatic CH in-plane bending is much more likely due to CH_3 .

5.1.4.2 Spectrum LC4b--

"C" correctly identified H_2O in KBr ($3600\text{--}3200\text{ cm}^{-1}$), unsaturated CH (3050 cm^{-1} , 3020 cm^{-1}), saturated CH (2930 cm^{-1} , 2850 cm^{-1}), aromatic ring (1619 cm^{-1} , 1597 cm^{-1} , 1558 cm^{-1}), and CH_3 (1450 cm^{-1} , 1383 cm^{-1} , 1364 cm^{-1}) structures.

5.1.4.3 Spectrum LC5a--

"C" correctly identified H_2O in KBr ($3700\text{--}3100\text{ cm}^{-1}$), secondary amine (3420 cm^{-1}), unsaturated CH (3045 cm^{-1}), saturated CH (2975 cm^{-1} , 2930 cm^{-1}), aromatic ring (1625 cm^{-1} , 1495 cm^{-1}), and CH_3 (1470 cm^{-1}) structures.

As in LC4a, the band at 1380 cm^{-1} , which was described as being due to 9-ethyl carbazole, could be described as being due to CH_3 .

5.1.4.4 Spectrum LC5b--

"C" correctly identified H_2O in KBr ($3700\text{--}3150\text{ cm}^{-1}$), unsaturated CH (3050 cm^{-1}), aromatic ring (1620 cm^{-1} , 1587 cm^{-1} , 1560 cm^{-1}), and quinone (1675 cm^{-1}) structures.

5.1.4.5 Spectrum LC6a--

"C" correctly identified H_2O in KBr ($3700\text{--}3100\text{ cm}^{-1}$), NH ($3600\text{--}2200\text{ cm}^{-1}$), carbonyl (1640 cm^{-1}), and aromatic ring (1590 cm^{-1} , 1540 cm^{-1}) structures.

"C" did not consider that the $3600\text{--}3350\text{ cm}^{-1}$ region was due to OH. A medium band at about 1240 cm^{-1} was not interpreted. An appropriate interpretation would have been to describe the band as being due to C-O of aromatic alcohol. Bands at 1160 cm^{-1} and 1100 cm^{-1} , which were not interpreted, are probably due to C-O structures also.

5.1.4.6 Spectrum LC6b--

"C" correctly identified the H_2O in KBr ($3650\text{--}3150\text{ cm}^{-1}$), OH of acid ($3500\text{--}2000\text{ cm}^{-1}$), aromatic ring (1590 cm^{-1} , 1565 cm^{-1}), C=O of ketone (1710 cm^{-1}), and C=O of acid (1680 cm^{-1}) structures. Other bands used to identify acid were 1425 cm^{-1} , 1290 cm^{-1} , and 914 cm^{-1} .

"C" did not interpret the bands at 1240 cm^{-1} and 1015 cm^{-1} , which could be interpreted as being due to the C-O-C of an ether.

5.1.5 Contractor D

5.1.5.1 Spectrum LC4a--

"D" correctly identified the presence of unsaturated CH ($3100\text{--}3000\text{ cm}^{-1}$) and aromatic ring (1620 cm^{-1} , 1530 cm^{-1}) structures.

"D" failed to assign a 2920 cm^{-1} band, which most likely arises from saturated CH. A band at 3420 cm^{-1} was described as being due to OH; this band, most likely, is a result of H_2O in the KBr. Bands at 1710 cm^{-1} and 1690 cm^{-1} were described as being due to ester and ketone, respectively. Carbonyl compound contamination could be responsible for these bands, though it is more probable that they are summation or overtone bands. Bands at 1450 cm^{-1} and 1390 cm^{-1} were described as being due to unsaturated CH. This assignment is not unreasonable though the band is most likely due to methyl groups in the mixture.

5.1.5.2 Spectrum LC4b--

Again "D" correctly identified the presence of unsaturated CH (3050 cm^{-1}) and aromatic (1530 cm^{-1} , 1500 cm^{-1}) structures.

As in the case of spectrum LC4a, bands at 2930 cm^{-1} and 2850 cm^{-1} (saturated CH), and 1385 cm^{-1} (CH_3) were not assigned. A band at 1450 cm^{-1} was described as being due to unsaturated CH. This assignment is not unreasonable though the band is most likely due to CH_3 .

5.1.5.3 Spectrum LC5a--

"D" correctly identified the presence of aromatic NH (3410 cm^{-1}), unsaturated CH (3030 cm^{-1}), and aromatic (760 cm^{-1} , 730 cm^{-1}) structures.

A broad band in the $3600\text{--}3200\text{ cm}^{-1}$ region that was not assigned most likely arises from H_2O in the KBr. Bands at 2975 cm^{-1} and 2930 cm^{-1} were not assigned; they should have been described as being due to saturated CH. Bands at 1450 cm^{-1} and 1380 cm^{-1} were described as being due to unsaturated CH, although they probably are due to CH_3 . Other bands at 1600 cm^{-1} , 1480 cm^{-1} , 1470 cm^{-1} , 1340 cm^{-1} , and 1230 cm^{-1} , described as being due to unsaturated CH, are due to aromatic stretch and/or NH bending.

5.1.5.4 Spectrum LC5b--

"D" correctly identified a band at 3500 cm^{-1} as being due to H_2O . Also correctly identified were unsaturated CH (3025 cm^{-1}) and aromatic (1620 cm^{-1}) structures.

A band at 1670 cm^{-1} was described as being due to a ketone. A more appropriate designation, based on the wavenumber, would have been to describe this band as being due to a conjugated ketone or a quinone. Another band at 1510 cm^{-1} was described as being due to C-N or (cyclic)-N structures. The wavenumber seems high for this structure and the band would more appropriately be described as being due to aromatic or heteroaromatic ring stretch.

5.1.5.5 Spectrum LC6a--

"D" correctly identified the presence of OH and/or NH (3120 cm^{-1}), aromatic C=O (1650 cm^{-1}), and aromatic ring (1100 cm^{-1} , 785 cm^{-1} , 730 cm^{-1}) structures.

"D" described a band at 1600 cm^{-1} as being due to C-O or aromatic C=O. This wavenumber is low for such an assignment and it is likely that the 1600 cm^{-1} band results from aromatic or heteroaromatic ring stretching. It should be added, however, that wavenumbers can be lower than expected due

to the "shifting" effect of molecular substitution. Another band at 1245 cm^{-1} was described as being due to aromatic C=O. More likely it is due to C-O of aromatic alcohol. A strong band at 1160 cm^{-1} , which was not assigned, is probably due to C-O of phenol or C-N structure. Another strong band at 1100 cm^{-1} , which was described as being due to aromatic rings, is also probably due, in part, to C-O structures.

5.1.5.6 Spectrum LC6b--

"D" correctly identified the C=O of ketone (1700 cm^{-1}), unsaturated CH (3000 cm^{-1}), and C-O-C of ether (1240 cm^{-1}) structures.

A serious omission is lack of identification of an acid. Carboxylic acid is strongly indicated by bands at 1680 cm^{-1} (C=O structure), 1430 cm^{-1} and 1240 cm^{-1} (coupling of OH bend and C-O stretch of a carboxylic acid dimer), and 915 cm^{-1} (OH out-of-plane bending of the acid dimer). As noted, the band at 1240 cm^{-1} can be ascribed either to a cyclic ether or an acid. A weak band at 1015 cm^{-1} not assigned by "D" supports an ether identification.

"D" assigned bands at 1190 cm^{-1} and 1160 cm^{-1} as being due to the C-O-C structure of ring ether. The wavenumbers appear too high for the antisymmetric C-O-C stretch which normally occurs in the range $1150\text{-}1070\text{ cm}^{-1}$ though substitution could result in such a shift; C-O of an aromatic alcohol would be a more appropriate assignment. "D" also assigned a strong band at 1300 cm^{-1} as being due to C-O-C. The value is somewhat high for such an assignment, though not out of line. The strong bands at 1710 cm^{-1} and 1680 cm^{-1} point, however, to the 1300 cm^{-1} band resulting from coupling between in-plane OH bending and C-O stretching of a carboxylic acid dimer.

5.2 IR ANALYSIS OF TEST SAMPLES

5.2.1 Introduction

In this second phase of the study, samples were prepared and sent to the participating contractors for IR/LRMS analysis. As explained in the introduction, the intent was to study approaches to measurement as well as interpretation. The samples, which included two synthetic samples representing LC fractions 5 and 6 and also a coal tar sample, are described in Section 4. The results of measurement and spectral interpretation are presented in Tables B7 and B8 and the RTI evaluation of these results is presented below.

5.2.2 IR Measurement

The approaches to measurement varied somewhat among contractors. "A" prepared the sample in a KBr pellet. "B" deposited a sample film on a NaCl plate while "D" smeared a portion of sample across a NaCl plate. "C" used a KBr pellet that had been prepared from an acetone-sample-KBr slurry. "A", "C", and "D" obtained spectra with grating spectrophotometers while "B" used a Fourier Transform (FT) IR spectrometer.

The quality of the LC5 and LC6 spectra was generally similar. The KBr technique ("C" and "A") resulted in good resolution below 2000 cm^{-1} but weak, broad signals above 2000 cm^{-1} . The salt plate technique, however, resulted in good resolution above 2000 cm^{-1} , with small bands as well as shoulders clearly revealed. Below 2000 cm^{-1} , the "C" spectra were generally superior to the others. For example, distinct sharp bands were noted in the "C" spectrum LC5 at 1658 and 1674 cm^{-1} whereas the "A" and "D" spectra revealed weak broad bands in this region, which only indicate the possibility of two peaks. The same is true for several shoulders on a signal from LC5 at 1500 cm^{-1} . The "B" FTIR spectra show very sharp bands below 2000 cm^{-1} . However, the spectra are plotted on a type of graph paper which apparently crowds the bands so that optimum resolution is not realized. (It should be noted that this study does not permit a comparison of advantages or disadvantages of IR vs. FTIR.)

Bands clearly from the same molecular source varied in terms of both spectrum location and wavelength assignment. Locations of a medium-strong band in LC5 were observed by RTI as 1412 cm^{-1} ("A"), 1418 cm^{-1} ("B"), 1412 cm^{-1} ("C"), and 1420 cm^{-1} ("D") and were assigned as 1410 cm^{-1} ("A"), 1417 cm^{-1} ("B"), 1412 cm^{-1} ("C"), and 1430 cm^{-1} ("D"). Similarly, locations of a medium-strong band in LC6 were observed as 1711 cm^{-1} ("A"), 1720 cm^{-1} ("B"), 1715 cm^{-1} ("C"), and $\sim 1720\text{ cm}^{-1}$ ("D"), and were assigned as 1710 cm^{-1} ("A"), 1720 cm^{-1} ("B"), 1715 cm^{-1} ("C"), and 1700 cm^{-1} ("D"). "D's" band in this case was a broad band composed of two unresolved bands; the apparent broadness was apparently due to overloading the plate.) Finally, the relative intensities of the bands observed in the spectra produced by each contractor are generally similar to those produced by the other contractors.

5.2.3 IR Interpretation

The approaches to interpretation of the spectra obtained by the contractors varied in both major and minor ways. "A" generally interpreted only the medium and strong bands while "D" interpreted a greater number of the weak bands, as well as the strong bands. "B" interpreted several of the bands in the coal tar spectra but almost none of the bands in the spectra obtained with samples LC5 and LC6. "C", however, interpreted most of the bands in the coal tar spectra and essentially every band in their spectra from LC5 and LC6. The vast majority of "C's" interpretations of LC5 and LC6 data were not direct interpretations of the spectral bands but rather assignments of bands to certain compounds after these compounds had been identified by LRMS.

5.2.4 Contractor A

5.2.4.1 Mixture LC5--

This mixture contained aromatic ring and methylene structure (fluorene and 2,3-benzofluorene), heterocyclic nitrogen structure (7,8-benzoquinoline, 1,10-phenanthroline, and phenazine), alkyl structure (2,6-dimethyl quinoline), and carbonyl structures (anthrone).

"A" correctly identified the presence of unsaturated CH (3050 cm^{-1}), C=O of conjugated ketone (1670 cm^{-1}), and aromatic ring (1610 cm^{-1} , 1585 cm^{-1}) structures.

"A" described a medium band at 1310 cm^{-1} as being due to the C-N of an aromatic secondary amine. This assignment, though erroneous, is not unreasonable for the band measured. Indeed, the 1310 cm^{-1} band in "A's" spectrum is considerably larger than that found in the other contractors' spectra, which may have contributed to this error. However, if secondary, aromatic amines were present, one would expect a stronger NH stretch band in the $3490\text{--}3450\text{ cm}^{-1}$ region. The weak band ($3600\text{--}3100\text{ cm}^{-1}$), described as being due to OH and/or NH, is probably due to H_2O in the KBr. "A" did not identify the presence of an alkyl group, perhaps because their spectrum is of low quality in the $3000\text{--}2900\text{ cm}^{-1}$ range.

5.2.4.2 Mixture LC6--

This mixture contained aromatic ring, carboxylic acid, and quinone structure (9-fluorenone, 1-fluorene carboxylic acid, and 9-fluorenone-4-carboxylic

acid); alkyl structure (2-methyl-1-tetralone and 2-methyl-1,4-naphthoquinone); and phenol structures (2-t-butyl phenol).

"A" correctly identified OH of carboxylic acid ($3300\text{--}2400\text{ cm}^{-1}$, 1415 cm^{-1}) and aromatic ring (1600 cm^{-1} , 1565 cm^{-1}) structures. Bands at 1305 cm^{-1} and 1295 cm^{-1} were correctly identified as being due to C-O of carboxylic acid (actually coupling between in-plane OH bending and C-O stretching of a carboxylic acid dimer).

"A" described a strong band at 1710 cm^{-1} as being due to C=O of acid. The band is actually due to C=O of ketone, though the "A"'s assignment is not unreasonable. The ketone band appears at 1710 cm^{-1} because most of the C=O structures in the mixture are part of unsaturated ring systems. "A" described a strong band at 1680 cm^{-1} as being due to a singly conjugated ketone or ortho, amino-substituted aromatic acid. This band is, in fact, due to the acid present. (An aromatic acid dimer normally has a C-O band at 1690 cm^{-1} .) "A" again appeared to miss identification of saturated CH because the spectrum is of low quality in the $3000\text{--}2900\text{ cm}^{-1}$ range. Other bands in "A's" spectrum that were not assigned and that indicate CH_3 are those at 1465 cm^{-1} and 1390 cm^{-1} . The CH_2 structure is indicated by bands at 1470 cm^{-1} and 728 cm^{-1} .

5.2.5 Contractor B

5.2.5.1 Mixture LC5--

"B" correctly identified the presence of fused-ring aromatic and heterocyclic nitrogen structures. Structural units missed included aliphatic and carbonyl structures. These were missed primarily because many bands were not interpreted. Important bands not used were 2950 cm^{-1} (aliphatic), 2920 cm^{-1} (aliphatic), 1670 cm^{-1} (carbonyl), 1445 cm^{-1} (aliphatic), 1360 cm^{-1} (aliphatic), and 1290 cm^{-1} (C-C-C bending and C-C stretching of aromatic carbonyl).

5.2.5.2 Mixture LC6--

"B" correctly identified the presence of an aromatic keto-acid. Alkyl and phenolic structures were missed. Again the problem is assumed to arise, in part, from incomplete utilization of available information. Bands apparently not used included those at 2950 cm^{-1} and 2920 cm^{-1} (aliphatic), 1468 cm^{-1} and 1392 cm^{-1} (aliphatic), and 1260 cm^{-1} (phenol).

5.2.6 Contractor C

5.2.6.1 Mixture LC5--

"C" correctly identified the presence of aromatic CH ($3100-3000\text{ cm}^{-1}$), C=O of quinone (1674 cm^{-1}), and aromatic ring (1614 cm^{-1}) structures. Heterocyclic nitrogen and alkyl structures were indicated through listing of specific compounds identified by LRMS.

"C" did not indicate directly the presence of alkyl structures. These could have been missed due to the low quality of the spectrum in the $3000-2900\text{ cm}^{-1}$ range.

5.2.6.2 Mixture LC6--

"C" correctly identified the presence of OH of carboxylic acid ($3250-2200\text{ cm}^{-1}$), C=O of ketone (1715 cm^{-1}), C=O of carboxylic acid (1683 cm^{-1}), and aromatic ring (1609 cm^{-1} , 1598 cm^{-1}) structures.

"C" did not identify the presence of phenol or alkyl structures. Alkyl structures again may have been missed due to the low quality of the spectrum in the $3000-2900\text{ cm}^{-1}$ range. Other bands in the spectrum indicating the presence of the CH_3 group are found at 1463 cm^{-1} and 1390 cm^{-1} . A band at 1190 cm^{-1} indicates the presence of phenol, though it was not described as such.

5.2.7 Contractor D

5.2.7.1 Mixture LC5--

"D" correctly identified the presence of saturated CH (2975 cm^{-1} , 2957 cm^{-1} , 2910 cm^{-1}), aromatic ring (1600 cm^{-1} , 1590 cm^{-1}), and nitrogen-containing, aromatic ring (1510 cm^{-1}) structures. Ketone was correctly described as being present, though the C=O band in the $1655-1665\text{ cm}^{-1}$ region was described as being due to C-O.

Phenol was described as being present, though it is not. However, a medium, broad band at 3400 cm^{-1} was noted in "D's" spectrum, which was described as being due to OH. This is reasonable, and the OH assignment is supported by other information; that is, description of a band at 1214 cm^{-1} as being due to phenolic C-O.

"D" described bands at 1360 cm^{-1} , 1340 cm^{-1} , 1330 cm^{-1} , 1315 cm^{-1} , 1220 cm^{-1} , and 1210 cm^{-1} as being due to C-O of ring alcohol. These wave number values appear to be too high for this assignment, especially since

any unsaturation present will bring the wave number value down below the expected alcohol range of $1150\text{--}1050\text{ cm}^{-1}$.

"D's" interpretation tends to show a bias toward nitrogen-containing structures. Bands at 1970 cm^{-1} and 1920 cm^{-1} were described as being due to NH but actually were due to aromatic summation bands. Bands at 1600 cm^{-1} and 1590 cm^{-1} were described as being due to phenyl-N, C-N, or C=C (conjugated) structures but were due to aromatic ring stretching. Another band at 1560 was described as being due to phenyl-N but is most likely due to aromatic ring stretch. Finally, a band at 1430 cm^{-1} was described as being due to C-N but is most likely due to CH structure.

5.2.7.2 Mixture LC6--

"D" correctly identified the presence of OH of carboxylic acid (3000 cm^{-1}), saturated CH (2680 cm^{-1} , 2580 cm^{-1}), and aromatic ring (1455 cm^{-1}) structures.

"D" described a band at 1700 cm^{-1} as being due to C=O of acid, which is not unreasonable. However, the band at 1700 cm^{-1} in "D"'s spectrum is composed of two bands, one at 1710 cm^{-1} and another at 1680 cm^{-1} , that were not resolved due to overloading of the salt plate. In this sample, the band at 1710 cm^{-1} was due to quinone and the band at 1680 cm^{-1} was due to aromatic carboxylic acid and, probably, quinone.

"D" described a band at 1610 cm^{-1} as being due to doublet C=C or amide-NH and another band at 1570 cm^{-1} as being due to C-NH. They are, however, most likely the result of ring stretching. "D's" interpretation may have been influenced by the fact that the bands were strong; they were weak or medium in the other contractors' spectra. The bands were strong in "D's" spectrum apparently because of overloading the salt plate.

"D" described bands at 1090 cm^{-1} and 1082 cm^{-1} as being due to a C-N-C ring structure. The 1090 cm^{-1} band is most likely due to C-O of phenol as is the 1082 cm^{-1} band.

5.3 IR ANALYSIS OF TAR DERIVED FROM COAL GASIFICATION

A sample of tar derived from coal gasification was sent to each participating contractor to be analyzed using the Level 1 liquid column chromatography procedure (LC) and IR/LRMS. Only the results of LC fractions, 4, 5, and 6 were to be reported. The contractors' interpretation results are pre-

sented in Tables B-9, B-10, and B-11 and the RTI interpretation of these results is presented below.

5.3.1 Contractors' Spectra

The spectra submitted by the contractors were examined for general quality and for similarities and differences.

There were few peaks present in the tar spectra in comparison to the number of peaks found with the synthetic mixture spectra. For example, the spectrum from LC5a (six components) contains about 50 bands compared to 20 in "A's" spectrum from TAR/LC5. The bands in these spectra were generally medium or weak, and were also broad. The spectra presented by "A", "B", and "D" were very similar for TAR/LC4, TAR/LC5, and TAR/LC6. Another observation was that the spectra representing each of the different LC fractions were very similar to one another. That is, except for changes in band intensity and the appearance or disappearance of minor bands, spectra for samples TAR/LC4, TAR/LC5, and TAR/LC6 appear to be nearly identical. Each of the fractions shows relatively large amounts of OH/NH and CH_2/CH_3 structure, and moderate amounts of aromatic and $\text{C}=\text{O}$ structure.

The spectra from "C" showed some of these same structures except these spectra were weaker than those from the other contractors, and also showed fewer bands. "A's" spectra for TAR/LC4 and TAR/LC5 each showed 15 to 20 bands compared to about 5 and 10 bands, respectively, for these two spectra submitted by "C". "C's" spectra for TAR/LC6 were generally more like the spectra for TAR/LC6 submitted by the other contractors.

5.3.2 Contractor A

5.3.2.1 TAR/LC4--

From GC analysis of the tar sample, LC4 would be expected to contain benzothiophene, dibenzofuran, and carbazole. From the IR/LRMS analyses, it is apparent that other unidentified compounds are also present.

Assignments of unsaturated CH (3050 cm^{-1}), saturated CH (2950 cm^{-1} , 2925 cm^{-1} , 2850 cm^{-1} , 1450 cm^{-1} , 1375 cm^{-1}), and OH/NH ($3600\text{--}3100\text{ cm}^{-1}$) are all reasonable. A band at 1720 cm^{-1} is described as due to $\text{C}=\text{O}$ of conjugated ester, aliphatic aldehyde or dialkyl ketone. "A" supports the aldehyde assignment as reasonable by describing a small band at 2740 cm^{-1} as being due to C-H of the CHO moiety. "A" supports the ester assignment by describ-

ing bands at 1320 cm^{-1} and 1230 cm^{-1} as being due to C-O of the ester. One would expect the bands at 1320 cm^{-1} to be much stronger than the 1720 cm^{-1} and 1230 cm^{-1} bands, which is not the case. An ester is still a possibility, however, as the bands at 1720 cm^{-1} and 1230 cm^{-1} could be due, in part, to other structural species.

"A" described a band at 1695 cm^{-1} as being due to acid, ketone, and/or aromatic aldehyde. The ketone and aldehyde assignments are reasonable, though the aldehyde would be expected to be a minor component due to the weakness of the band at 2740 cm^{-1} relative to the band at 1695 cm^{-1} . The acid is not a strong possibility due to the great weakness of bands at 1420 cm^{-1} (coupling between in-plane O-H bending and C-O stretching of dimer) and 920 cm^{-1} (O-H out-of-plane bending of dimer).

"A" assigns bands at 1600 cm^{-1} , 1485 cm^{-1} , and 1450 cm^{-1} as being due, at least in part, to aromatic C=C structure, which is reasonable. Assignment of bands in the 1000 to 1300 cm^{-1} as being due to C-O of aromatic alcohols and/or unsaturated CH is also reasonable. The band at 1600 cm^{-1} is also assigned as possibly due to C=O--HO (hydrogen bonded ketone), which is reasonable.

5.3.2.2 TAR/LC5--

From GC analysis of the tar sample, LC5 would be expected to contain some of the compounds found in LC4 and LC6, including carbazoles, pyridines, acridines, quinolines, and phenols.

The assignments made for this fraction are nearly identical to those made for TAR/LC4. Again, OH/NH ($3600 - 3100\text{ cm}^{-1}$), unsaturated CH (3050 cm^{-1}), saturated CH (2955 cm^{-1} , 2925 cm^{-1} , 2860 cm^{-1} , 1450 cm^{-1} , 1375 cm^{-1}), and aromatic C=C (1600 cm^{-1} , 1500 cm^{-1} , and 1450 cm^{-1}) structure assignments are made and are reasonable. Other reasonable assignments include aldehyde (2740 cm^{-1} , 1725 cm^{-1}) and ketone (1725 cm^{-1} , 1695 cm^{-1} , $1225 - 1075\text{ cm}^{-1}$ [unresolved]).

Assignment of an ester (1725 cm^{-1}) is more reasonable for this fraction in that relatively strong bands are found at 1265 cm^{-1} , 1235 cm^{-1} , and 1190 cm^{-1} (symmetric and asymmetric stretching of C-O-C). Assignment of an acid (1695 cm^{-1}) is not very reasonable for the same reasons put forth in Section 5.3.2.1.

"A" described the 3600 to 3100 cm^{-1} range as being due to phenol and the 1310 to 1110 cm^{-1} range as being due to C-O of aromatic alcohol. Both are reasonable assignments. Also, these bands are larger and broader than those found in the spectrum from TAR/LC4, indicating an increase in the phenolic character (and also an increase in polar character).

5.3.2.3 TAR/LC6--

From GC analysis of the tar sample, LC6 would be expected to contain benzidine, alkyl pyridines, quinoline, alkyl quinolines, alkyl benzoquinolines, acridine, phenol, cresol, xylenols, isopropyl phenol, and trimethyl phenol.

"A" assigned essentially the same structures to TAR/LC6 as to TAR/LC5. That is, OH/NH (3600 - 3100 cm^{-1}), unsaturated CH (3050 cm^{-1}), saturated CH (2955 cm^{-1} , 2920 cm^{-1} , 2850 cm^{-1} , 1450 cm^{-1} , 1375 cm^{-1}), aromatic ring (1595 cm^{-1} , 1500 cm^{-1} , 1450 cm^{-1}) and aromatic OH structures (3600 - 3100 cm^{-1} , 1310 - 1110 cm^{-1}) were assigned. There is no noticeable band at 1720 cm^{-1} and so ester is not assigned. The band at 1690 cm^{-1} was described as being due to acid, ketone, and/or aldehyde. The aldehyde and ketone are reasonable possibilities. The acid is a greater possibility here than for TAR/LC4 and TAR/LC5 in that (1) the peak of the band in the 3600 to 3100 cm^{-1} region is shifted from 3400 cm^{-1} to 3300 cm^{-1} (indicating more intermolecular H-bonding); (2) the band at 1450 cm^{-1} in spectra for TAR/LC4 and TAR/LC5 is shifted to 1440 cm^{-1} (closer to the 1420 cm^{-1} band expected from coupling between in-plane O-H bending and C-O stretching of acid dimer); and (3) there is a stronger band at 940-920 cm^{-1} (O-H out-of-plane bending of acid dimer) than the spectra for TAR/LC4 and TAR/LC5.

5.3.3 Contractor B

As with the synthetic spectra and mixtures, "B" interpreted very few bands.

5.3.3.1 TAR/LC4--

"B" described this LC fraction as containing carbazole and/or N-alkyl carbazole, aliphatic hydrocarbons, and some carbonyl and nitrile. This interpretation is reasonable though it is not totally supported by the band-by-band interpretations reported by the contractor.

"B" described a band at 3052 cm^{-1} as being due to O-H stretch whereas it is due most likely to unsaturated CH. The broad band centered at 3400 cm^{-1} (due to OH/NH) was not listed on the report form. Bands at 2955 cm^{-1} , 2922 cm^{-1} , 2850 cm^{-1} , 1460 cm^{-1} , and 1375 cm^{-1} were properly described as being due to CH_2/CH_3 .

A band at 1605 cm^{-1} was described as being due to aromatic C=C or C=N; both are reasonable assignments. Other bands at 1490 cm^{-1} , 1460 cm^{-1} , and 1450 cm^{-1} , which are probably due, at least in part, to aromatic C=C, are not interpreted as such. Bands at $3600 - 3100\text{ cm}^{-1}$, 1325 cm^{-1} , 1270 cm^{-1} , 1235 cm^{-1} , and 1200 cm^{-1} , which all support aromatic alcohol, were not interpreted although the latter four were listed on the report form. The band at 1698 cm^{-1} was not interpreted on the report form though it apparently is the band responsible for the mention of the presence of carbonyl.

Bands that would support the carbazole assignments, including those at $3600 - 3100\text{ cm}^{-1}$ (N-H), 1325 cm^{-1} (C-N), 1270 cm^{-1} (C-N), 1120 cm^{-1} (cyclic C-N), and 750 cm^{-1} (ortho disubstitution of aromatic rings), were not interpreted as such.

5.3.3.2 TAR/LC5--

"B" described this LC fraction as containing fused-ring aromatic or heteroaromatic ring structures, aliphatic structures, and carbonyl structures. This assignment is reasonable, though again thorough band-by-band support is not presented.

"B" described a band at 3400 cm^{-1} as being due to OH, which is reasonable, though NH could also be responsible. Unsaturated CH (3040 cm^{-1}) and saturated CH (2955 cm^{-1} , 2922 cm^{-1} , 2860 cm^{-1} , 1450 cm^{-1} and 1375 cm^{-1}) structures are reasonably identified. Bands probably due to aromatic C=C (1595 cm^{-1} , 1490 cm^{-1} , 1540 cm^{-1}) are not described as such.

Carbonyl is indicated as present, though specific, possible structures such as C=O attached to an aromatic ring (the 1690 cm^{-1} band) or C=O connecting two aromatic rings (the 1660 cm^{-1} band) are not indicated. An unassigned band at 1270 cm^{-1} supports the ketone assignment (C-C-C bending and C-C stretching of $-\text{C}(\text{CO})-\text{C}-$). The bands at 3400 cm^{-1} (OH stretch) and at 1265 cm^{-1} , 1205 cm^{-1} , and 1195 cm^{-1} (C-O stretch) also support the presence of an aromatic alcohol, which was not indicated. Finally, unsaturated alde-

hyde is indicated by unassigned bands at 2730 cm^{-1} (C-H stretch) and 1690 cm^{-1} (C=O).

5.3.3.3 TAR/LC6--

"B" described this fraction as containing aromatic amine, phenol(s), and aliphatic hydrocarbon, all of which are reasonable assignments.

"B" described a broad band centered at 3320 cm^{-1} as being due to OH. NH is another possibility implied but not assigned to this band as such. Unsaturated CH (3055 cm^{-1}), saturated CH (2955 cm^{-1} , 2870 cm^{-1} , 2850 cm^{-1} , 1455 cm^{-1} , 1375 cm^{-1}), and phenol (1235 cm^{-1}) are all reasonable assignments. Other bands at 1315 cm^{-1} and 1353 cm^{-1} (O-H bend) and 1170 cm^{-1} (C-O stretch alcohol) support the phenol assignment but are not described as such. Bands at 1590 cm^{-1} and 1265 cm^{-1} were described as being due to amine. The strength of the band at 1590 cm^{-1} does imply that it is due to the N-H bending vibration of an -NH_2 structure and the band at 1265 cm^{-1} could be due to a C-N stretching vibration of a secondary amine. Bands at 1180 cm^{-1} and 1235 cm^{-1} could be due to C-N stretch of primary amine, though they are not described as such. It is difficult to identify a medium, broad band in the $900\text{-}640\text{ cm}^{-1}$ range (as would be expected for primary amine) due to the presence of several, overlapping, aromatic, out-of-plane C-H bending bands in this same region.

The band at 1590 cm^{-1} is certainly due, in part, to aromatic C=C structure, and could be due, in part, to aromatic C=N structure. The band at 1455 cm^{-1} is much stronger, however, than the band at 1370 cm^{-1} , indicating that the band at 1455 cm^{-1} is due more to aromatic C=C than CH_3 ; this indicates that the band at 1590 cm^{-1} is due in part (perhaps a major part) to aromatic C=C.

Finally, other bands not interpreted include a band at 1685 cm^{-1} that is most likely due to C=O attached to aromatic ring(s) and bands at 1235 cm^{-1} and 1040 cm^{-1} that indicate the presence of =C-O-C structure (aromatic or vinyl ether).

5.3.4 Contractor C

5.3.4.1 TAR/LC4--

"C" identified the presence of saturated CH (2960 cm^{-1} , 2925 cm^{-1} , 2865 cm^{-1} , 2853 cm^{-1} , 1435 cm^{-1} , 1379 cm^{-1} , and 1370 cm^{-1}), OH and/or H_2O in KBr ($3700\text{-}3000\text{ cm}^{-1}$), and C=O (1737 cm^{-1}), which is reasonable. The band at

1737 cm^{-1} was identified as possibly due to an ester, which is reasonable. Bands at 1100 cm^{-1} and 1160 cm^{-1} (stronger than the band at 1739 cm^{-1}) would support the ester assignment and be described as being due to C-O-C stretching, though they were not assigned as such.

"C" described bands at 1150 cm^{-1} , 1105 cm^{-1} , 1050 cm^{-1} , and 1020 cm^{-1} as being due to C-O of alcohol(s), which is consistent with the broad, strong band in the 3700-3000 cm^{-1} range. These bands could also be due to ethyl, propyl, or butyl groups, which would be consistent with the other strong bands identified as being due to saturated CH.

5.3.4.2 TAR/LC5--

"C's" spectrum for this LC fraction was similar to that for TAR/LC4, except that spectrum bands were generally weaker.

"C" identified the presence of H_2O in KBr (3050 -3150 cm^{-1}), saturated CH (2955 cm^{-1} , 2925 cm^{-1} , 2865 cm^{-1} , 2853 cm^{-1} , 1448 cm^{-1} , and 1370 cm^{-1}), and aromatic ring structure (1600 cm^{-1} , 740 cm^{-1}). "C" described a band at 1685 cm^{-1} as possibly being due to C=O of conjugated ketone or amide I, which is reasonable.

Though not described as such, bands at 3700-3100 cm^{-1} , 1600 cm^{-1} , 1260 cm^{-1} , and 750 cm^{-1} indicate the presence of a primary amine attached to an aromatic ring.

5.3.4.3 TAR/LC6--

The bands in this spectrum were much stronger than the spectra from TAR/LC4 and TAR/LC6.

Assignments of OH of H_2O , alcohol, phenol, or carboxylic acid (3700-2200 cm^{-1}), unsaturated CH (3100-3000 cm^{-1}), saturated CH (2955 cm^{-1} , 2923 cm^{-1} , 2870 cm^{-1} , 2853 cm^{-1} , 1460 cm^{-1} , 1448 cm^{-1} , and 1373 cm^{-1}), aromatic ring (1598 cm^{-1} , 1506 cm^{-1} , 1485 cm^{-1} and 1460 cm^{-1}), and C-O of phenol (1265 cm^{-1} , 1220 cm^{-1}) are all reasonable. "C" supports the argument for the presence of carboxylic acid via the assignment of the band at 1685 cm^{-1} as being due to C=O of aromatic acid. The argument for the presence of carboxylic acid is weakened by the weakness of the bands at 1420 cm^{-1} (coupling between in-plane O-H bending and C-O stretching of acid dimer) and 920 cm^{-1} (OH out-of-plane bending of dimer). Alternatively, the 1685 cm^{-1} band could result from C=O attached to an aromatic structure; also, the intermolecular

H-bonding band noted in the 3500-2500 cm^{-1} range could be a result of interaction between phenols and ketones present.

Finally, "C" described a band at 1030 cm^{-1} as being due to C-O of $-\text{CH}_2\text{OH}$. This is not unreasonable though the band could be due to ethyl or propyl groups, which would be consistent with the large number of saturated CH bands identified.

5.3.5 Contractor D

5.3.5.1 TAR/LC4--

"D" describes this spectrum as indicating the presence of ring structures substituted with C-O, C=O, and OH groups. This is reasonable, though aliphatic structures are also definitely present.

Assignments of OH (3600-3100 cm^{-1}), unsaturated CH (3050 cm^{-1}), saturated CH (2950 cm^{-1} , 2910 cm^{-1} , 2850 cm^{-1} , 1450 cm^{-1} and 1375 cm^{-1}); and aromatic C=C (1600 cm^{-1}) are reasonable.

"D" assigned a band at 1695 cm^{-1} as being due to C=O, which is reasonable. A band at 1660 cm^{-1} was described as being due to C=O in $=\text{C}(\text{R})=\text{O}$; a better assignment would be C=O for $=\text{C}-\text{C}(=\text{O})-\text{C}=$. A band at 1490 cm^{-1} was described as being due to CH_2 ; a better assignment would be aromatic C=C. A band at 1320 cm^{-1} was described as being due to $\text{O}=\text{O}$; it would probably be better described as being due to bend of OH of phenol. Bands at 1275 cm^{-1} , 1235 cm^{-1} , and 1210 cm^{-1} are described as being due to phenol, which is reasonable.

5.3.5.2 TAR/LC5--

"D" described this fraction as essentially identical to TAR/LC4. Assignments of OH (3600-3100 cm^{-1}), unsaturated CH (3050 cm^{-1}), saturated CH (2960 cm^{-1} , 2925 cm^{-1} , 2850 cm^{-1} , 1450 cm^{-1} and 1375 cm^{-1}), C=O (1685 cm^{-1}), aromatic ring (1600 cm^{-1}), and phenol (1270 cm^{-1} , 1215 cm^{-1}) are all reasonable. A band at 1500 cm^{-1} is described as being due to CH_2 , though it is due more likely to aromatic C=C.

5.3.5.3 TAR/LC6--

"D" describes this LC fraction as containing ester, ketone, carboxylic acid, heterocyclic nitrogen, and fused aromatics. The presence of ester is questionable, though, and carboxylic acid, if present at all, is present at low concentrations.

Assignments of OH ($3600\text{--}2300\text{ cm}^{-1}$), unsaturated CH (3050 cm^{-1}), saturated CH (2960 cm^{-1} , 2920 cm^{-1} , 2850 cm^{-1} , 1450 cm^{-1} and 1375 cm^{-1}), C-O of phenol (1270 cm^{-1} , 1230 cm^{-1}), and aromatic ring (1600 cm^{-1}) are all reasonable.

The assignment of ester as present is apparently based on the broadness of the band centered at 1695 cm^{-1} . The base of the band extends to 1800 cm^{-1} with a shoulder at about 1760 cm^{-1} . Bands arising from C=O of an ester range from 1720 cm^{-1} to 1770 cm^{-1} ; thus ester is a possibility. However, each of "D's" tar sample spectra show the C=O band centered at about 1695 cm^{-1} extending to about 1800 cm^{-1} , and this same broadness is found in other contractors' spectra. If the band centered at 1695 cm^{-1} is due, in part, to ester, then two bands, one very strong and the other strong relative to the ester C=O band, would be expected in the $1300\text{--}1050\text{ cm}^{-1}$ range. Such bands cannot be readily identified in the midst of other signals at 1190 cm^{-1} , 1230 cm^{-1} , 1270 cm^{-1} (C-O stretches), and 1360 cm^{-1} (O-H bend), which are apparently due to phenol.

The broadness of the band in the $3600\text{--}2200\text{ cm}^{-1}$ range indicates the presence of carboxylic acid as does the broadness of the band centered at 1695 cm^{-1} . Other bands at 1420 cm^{-1} (coupling between in-plane O-H bending and C-O stretching of acid dimer) and 920 cm^{-1} (O-H out-of-plane bending of acid dimer) appear very weak, however, indicating a low concentration of carboxylic acid. The broadness of the band in the $3600\text{--}2200\text{ cm}^{-1}$ range may be due to intermolecular H-bonding between other species present such as ketone and phenol, the latter being indicated by bands at $3600\text{--}3100\text{ cm}^{-1}$, 1360 cm^{-1} , 1260 cm^{-1} , 1230 cm^{-1} , and 1190 cm^{-1} .

Finally, "D" described a band at 1500 cm^{-1} as being due to CH_2 or C-N-C (a basis for the heterocyclic nitrogen compound assignment). This band is probably due, in part, to aromatic C=C. The CH_2 structure isn't a likely contributor to this band. One literature source describes C-N-C giving rise to a band at 1100 cm^{-1} but not 1500 cm^{-1} .

5.4 DISCUSSION OF RESULTS OF IR STUDIES

5.4.1 Infrared (IR) Measurements and Interpretation

5.4.1.1 IR Measurements--

Several factors of the IR measurement that affect final interpretation results were observed. The first of these concerns the type of instrument used. Grating instruments and a Fourier transform spectrometer were used in

this study. No significant difference in the resolution or band-to-noise ratio spectra generated by these different instruments was noted. Another concern was the method of sample preparation. In this study, two contractors placed their samples on salt plates and the other two prepared KBr pellets with the samples. It is noted that the spectra obtained with the salt plates show more and clearer bands above 2000 cm^{-1} than do those obtained with KBr pellets. This has an effect upon interpretation; for example, the presence of saturated CH structure, which is indicated by bands in the $3000\text{-}2900\text{ cm}^{-1}$ range, has been missed. This problem with KBr, which may be due to interaction with the KBr pellet, "pellet cloudiness," or loss of volatile species, needs to be investigated.

Another factor affecting final results is concentration of sample on the salt plate or in the KBr pellet. This concentration was not always optimized. It is true that sample quantity is often limited and thus small IR bands are unavoidable. Whenever possible, however, concentration of sample should be such that the largest band in the spectrum has an absorbance of about one. Overloading of the salt plate or KBr pellet was also observed to be a problem. When overloading occurs, the magnitude of the largest bands cannot be accurately estimated because their absorbances approach infinity. Such large bands occurring close to one another will not be resolved, leading to interpretation error. This has occurred with carbonyl bands from different species (e.g., acid, ester, ketone) that are all in the $1735\text{-}1680\text{ cm}^{-1}$ range. Another problem with large bands is that they result in inaccurate estimation of the relative magnitude of smaller bands. This leads to interpretation error also. For example, C-N results in a relatively large band due to its polarity. An OH band, which falls in the same wavelength range as the C-N band, is normally weak; overloading could cause an improperly large band from OH to be interpreted as a band from C-N.

A third factor affecting quality of interpretation is accuracy of band location. Variation in band location was observed to be due both to instrumental variation and inaccurate visual assignment of location. Variation among contractors as great as 10 cm^{-1} was noted for assignment of bands that were clearly arising from the same molecular source. It is essential that an IR instrument be calibrated regularly. Also, visual identification of band location must be made with great care and rounding off must be avoided.

5.4.1.2 IR Interpretation Results--

The accuracy level of the interpretation was generally acceptable. The levels of accuracy of identification of major structures indicated by spectra LC4a-LC6a and spectra acquired with sample LC5 and LC6 are as follows: "A"--75 $\pm$ 10 percent; "B"--60 $\pm$ 10 percent; "C"--80 $\pm$ 10 percent; and "D"--65 $\pm$ 10 percent. The uncertainty value, $\pm$ 10 percent, is a simple estimate based on the fact that some assignments can be incorrect, though still reasonable. As noted in Section 6, the error level increases with the LC fraction, but then so do the spectrum and/or sample complexity.

Several types of errors that resulted in a group not being identified, or a group not actually present being identified as such, were noted. These included simple assignment errors, assignments made that were reasonable or rational but not correct, failure to interpret bands, and failure to use alternate bands to support or refute assignments based on other bands.

5.4.1.2.1 Bands not used--Numerous bands were not used, as described in Section 5. Some of these were primary bands for structural groups, such as 1680 cm^{-1} for carbonyl; others were secondary bands for structural groups, such as 1385 cm^{-1} for CH_3 . Examples of data not used are presented in Table 28.

5.4.1.2.2 Errors in assignment--Errors in assignment were not often made; however, some errors are apparent. Examples of erroneous assignments are presented in Table 29.

5.4.1.2.3 Rational, though incorrect, assignments--As noted above, direct errors do not occur often. It is more likely that assignments will be made that are rational but are nevertheless in error. This occurs, of course, because different structures give rise to bands in the same wavelength regions. Examples of such errors are presented in Table 30.

5.4.1.2.4 Incomplete use of available information--The problems noted above could apparently be resolved if greater advantage were taken of complementary data available in most spectra. That is, most structures give rise to several bands that often have regular relationships in terms of magnitude and breadth. For example, the $\text{C}=\text{O}$ group in a $-\text{C}=\text{C}-\text{C}(=\text{O})-\text{O}-$ ester structure usually has a very strong band from $\text{C}-\text{O}$ in the 1300-1250 cm^{-1} range and a strong band from $\text{C}-\text{O}$ in the 1200-1050 cm^{-1} range. Such complementary bands serve both to support and refute assignments. Examples of such complementary data not used are:

TABLE 28. SELECTED EXAMPLES OF UNASSIGNED BANDS
FOUND IN VARIOUS SPECTRA

<u>Band not assigned, cm⁻¹</u>	<u>RTI assignment</u>
2930, 2850	Saturated CH
1680, 1670	Carbonyl
1430, 1240	Coupling of acid OH/C-O groups
1450, 1465, 1390, 1380, 1364	CH ₃
1240, 1160, 1100	C-O of alcohol
1015	C-O-C of ether

TABLE 29. SELECTED EXAMPLES OF ERRORS IN ASSIGNMENT OF BANDS

<u>Band, cm⁻¹</u>	<u>Apparently erroneous assignment</u>	<u>Apparently correct assignment</u>
1805	Carbonyl	Overtone or summation band
1600	Unsaturated CH	Aromatic C=C
1600	ϕ C=O	Aromatic C=C
1480, 1470	Unsaturated CH	CH ₃
1510	C-N	Aromatic C=C
1245	ϕ C=O	C-O of aromatic alcohol
3052	OH	Unsaturated CH

TABLE 30. SELECTED EXAMPLES OF RATIONAL, THOUGH
INCORRECT, ASSIGNMENTS

<u>Band, cm⁻¹</u>	<u>Erroneous assignment</u>	<u>Apparently correct assignment</u>
1715, 1690	Carbonyl	Overtone or summation bands
1710	C=O of ester	C=O of ketone
1710	C=O of acid	C=O of ketone
1280, 1240	C-O of aromatic alcohol	CH ₃
1235	C-O of aromatic alcohol	C-N of carbazole
1300	C-N of aryl amine	OH/C-O coupling
1310	C-N of secondary amine	C-C(=O)-C of ketone

TABLE 31. SELECTED EXAMPLES OF ALTERNATE REASONABLE ASSIGNMENTS

<u>Band, cm⁻¹</u>	<u>Assignment</u>	<u>Alternate assignment</u>
1050, 1020	C-O of alcohol	C-H of ethyl or propyl groups (as band at 3000-2900 cm ⁻¹ , 1450 cm ⁻¹ , and 1380 cm ⁻¹ large)
3650-3150	H ₂ O	OH or NH stretch
1600	Aromatic C=C	-NH ₂
1320	C=O of quinone	C-N stretch of amine and/or O-H bend of alcohol
1105	C-O of alcohol	C-N stretch of amine

1. A band at 1240 cm^{-1} is described as being due to an ester. There is no band at 1735 cm^{-1} ($\text{C}=\text{O}$ of ester), however, which refutes the 1240 cm^{-1} assignment.
2. A band at 1240 cm^{-1} is described as being due to C-O of ether. Another band at 1015 cm^{-1} , which is apparently due to symmetric stretch of C-O-C and which supports the 1240 cm^{-1} assignment, was not utilized.
3. A band at 1690 cm^{-1} is described as being due to an acid, ketone, or aldehyde. Several bands support the acid assignment but are not described as such. These include a broad band centered at 3300 cm^{-1} due to OH. Normally, the OH band is centered at $\sim 3400\text{ cm}^{-1}$ and the shift to 3300 cm^{-1} indicates more OH/C=O hydrogen bonding, which is typical of an acid. Another band centered at 1440 cm^{-1} is close to the band expected at 1420 cm^{-1} for coupling of O-H bend and C-O stretch of an acid. Finally, a band was observed in the $940\text{--}920\text{ cm}^{-1}$ range, which is close to the band expected at 915 cm^{-1} for O-H out-of-plane bending of an acid.
4. A band at 1590 cm^{-1} is described as being due to an amine. This band location is typical of a primary amine, which was not indicated. Bands at 1180 cm^{-1} and 1235 cm^{-1} , which could be the C-N stretch of a primary amine and which support the 1590 cm^{-1} assignment, were not utilized.
5. A band at 1737 cm^{-1} is described as being due to $\text{C}=\text{O}$ of an ester. Bands at 1160 cm^{-1} and 1100 cm^{-1} , which are stronger than the 1737 cm^{-1} band and thus could be symmetric or antisymmetric C-O-C stretching, thus support the 1737 cm^{-1} assignment but were not described as such.
6. A band at 1235 cm^{-1} was described as being due to phenol (i.e., C-O stretch of phenol). Bands at 1315 cm^{-1} and 1353 cm^{-1} , which could be due to O-H bend of phenol and thus support the 1235 cm^{-1} assignment, were not described as such.

5.4.1.2.5 Alternate assignments--In several of the preceding sections, assignment errors are noted. These errors were identifiable because the spectra were prepared from known mixtures of compounds. This is not the case with the tar sample, which has been only partially characterized, and only reasonableness of assignments can thus be judged. Examples of alternate, reasonable assignments are presented in Table 31.

5.4.2 Fundamental Problems in IR Interpretation

Two major problems complicate the interpretation task. The first is weakness and extent of band overlap found in real-world samples. The second is the disagreement among experts regarding band assignment.

5.4.2.1 Spectrum Problems--

Figure 17 shows a spectrum obtained from LC fraction 6 of the coal tar by one of the contractors. The bands are not as weak in this spectrum as they are in many real-world sample spectra. The overlap of bands, especially below 1800 cm^{-1} , is illustrative of what is often found in real-world sample spectra.

The breadth of the band centered at about 1690 cm^{-1} indicates the presence of several C=O-containing species including ketones and/or acids and/or esters, all of which are supported by other bands in the spectrum. An especially difficult region is that between about 1400 cm^{-1} and 1000 cm^{-1} . Bands found in this region include the following: CH of alkane; CH of aromatic systems; OH of alcohol; C-O of alcohol; C-O of esters; C-C-C bending and C-C stretch of -C(CO)-C- ; C-N stretch of amines; C-O of ether; and OH/C=O coupling of acids. Because of this overlap, decisions about these species must be based on complementary bands found in other parts of the spectrum and also other information about the sample, including LRMS data. Indeed, the appearance of the band envelope between 1000 cm^{-1} and 900 cm^{-1} indicates the presence of many overlapping bands. It may well be that these bands represent only a few types of compounds, but that the center of the bands arising from each molecule in a particular structure (e.g., ketone) varies slightly due to other aspects of the molecule's structure (e.g., size, bond order, atomic heterogeneity). Computer-assisted numerical resolution or deconvolution of the overlapping bands is one possible way to deal with this problem. Such data treatment would be expensive and difficult, and probably would not be cost-effective in terms of useful information collected.

5.4.2.2 Assignment Problems--

Another major difficulty discovered stems from disagreement regarding assignments. That is, on the basis of their experience and the reference materials used, the IR spectroscopists assign bands found at similar or equivalent wavelengths to different structures. Usually the alternate assignments are reasonable. Examples of alternate assignments are presented in Table 32.

Indeed, one of the spectroscopists exhibited a bias toward N-containing structures. Assignments of C-N and N-H were often made whereas others

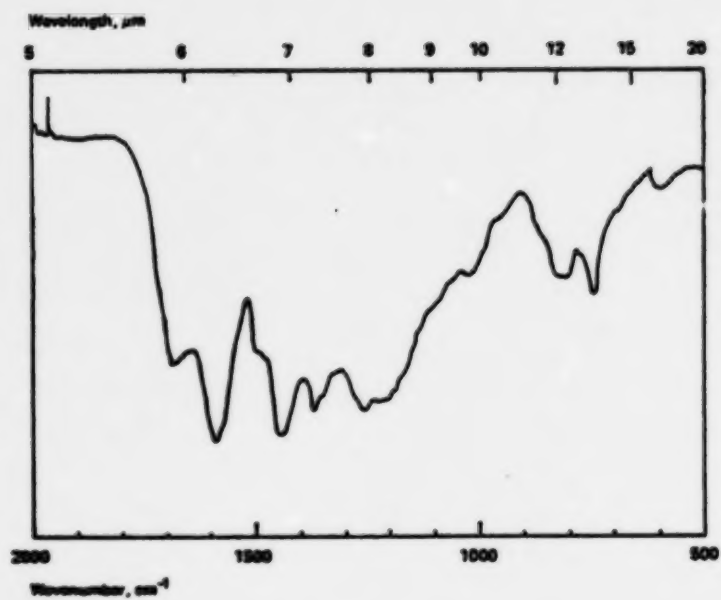


Figure 17. IR spectrum, LC6, coal tar sample.

TABLE 32. SELECT EXAMPLES OF DIFFERENT ASSIGNMENTS MADE FOR THE SAME BAND FROM THE SAME SPECTRUM

Band, cm^{-1}	Assignments		
	#1	#2	#3
1450	Aromatic C=C	C-H, in-plane bend	--
1300	Aryl amine	C-O-C	C-O stretch of COOH
910	C-H out-of-plane bend	OH out-of-plane bend of COOH	Cyclic ether
1710	C=O of acid	C=O of ketone	--
3600-3200	OH or NH stretch	H ₂ O in KBr	--

TABLE 33. WAVELENGTH RANGES INDICATED FOR DIFFERENT STRUCTURES AS FOUND IN THREE DIFFERENT REFERENCE SOURCES

Structure	Reference Source		
	N. B. Colthup (1950)	Dow Chemical	Nakanishi (1962)
OH bend of alcohol	1260-1460 cm^{-1}	--	1500-1200 cm^{-1}
C-O stretch of alcohol	1290-1000 cm^{-1}	1260-980 cm^{-1}	1200-1000 cm^{-1}
NH bend of primary amine	1640-1560 cm^{-1}	1665-1625 cm^{-1}	1640-1560 cm^{-1}
Aromatic C=C	1650-1550 cm^{-1} 1540-1450 cm^{-1}	1665-1615 cm^{-1} 1515-1370 cm^{-1}	1600-1450 cm^{-1} --
C-O-C of aliphatic ether	1175-1055 cm^{-1}	1140-1090 cm^{-1}	1200-1040 cm^{-1}
C=N stretch	1700-1590 cm^{-1}	1630-1590 cm^{-1}	1690-1640 cm^{-1}

assigned OH, C-O, C=C, or CH to these same bands. In this case, the spectroscopist's early training was with compounds containing nitrogen.

Even reference works produced by experts show disagreement. Table 33 illustrates this fact. It appears in this study that the variation in ranges shown in Table 33 does not lead to very many errors because the spectroscopists apparently rely more on their experience than on reference works of this sort.

5.4.3 Approaches to Interpretation of IR Spectra

Experience of the spectroscopist has been mentioned as a factor affecting the quality of the interpretation results. Other factors affecting this quality include approaches taken during interpretation and the time spent on each spectrum. These factors were investigated through personal interviews with each of the four IR spectroscopists who participated in this study. The information collected during these interviews is presented in the following subsections.

5.4.3.1 Contractor A

IR analysis is carried out by a small group at "A". Technicians obtain the spectra and a spectroscopist with 7 years of experience interprets the spectra.

The spectroscopist first studies the spectra looking for major bands that clearly indicate the presence of OH, C=O, aliphatic, and/or aromatic structures. When structures such as these are indicated by major bands, the spectroscopist examines the spectra for other, secondary bands that would support or refute the initial indications. It is at this time that the spectroscopist consults texts such as those by Rao (1963) and Colthup (1964) to determine which secondary bands found in the spectrum best match the major bands present. It is quite possible, too, that the small and/or secondary bands will not be found to support any major bands; that is, they probably indicate structures not indicated by the major bands. During the interpretation process, the IR spectroscopist continually interacts with the mass spectroscopist to compare findings and to determine whether the IR and MS data support or refute one another. When either an IR or MS result strongly indicates the presence or absence of a particular structure, and the other method does not do so, this strong indication will be the determining factor in re-

porting the sample contents. Finally, the IR spectroscopist usually spends about 1 hour on normal environmental assessment sample spectra, which, in fact, was the time spent on the spectra included in this study.

5.4.3.2 Contractor B

At "B", three IR spectroscopists have been involved in Level 1 work. One has 20 years of experience, the second has 3 years of experience and the third has 6 months of experience. Each of the three spectroscopists interpreted the spectra LC4a-LC6b, and the spectroscopist with 6 months' experience measured and interpreted the spectra for the two synthetic samples (LC5 and LC6) and the tar sample. Each of the spectroscopists identified about 50 percent of the structures indicated by spectra LC4a-LC6b, with the most experienced spectroscopist identifying approximately 10 percent more of the structures indicated than the other two. It appears that this low level of achievement does not accurately reflect the abilities of these spectroscopists or their levels of experience. Rather it seems that this low level of achievement results from lack of thoroughness of interpretation. As noted in Section 5, many bands simply were not interpreted.

The spectroscopist who analyzed the samples (LC5, LC6, and tar) will be doing much of the Level 1 work in the future; therefore this person's approach to interpretation is presented. This spectroscopist first looks at the major bands in a spectrum and attempts to assign structures characteristic of classes or categories; for example, carbonyl, aromatic structure or aliphatic structure. The minor bands, which would support or refute these class assignments, are then studied. The spectroscopist relies on memory for assignment of the major bands but uses reference books (e.g., L. J. Bellamy, 1958) or tables and/or calls upon the most experienced spectroscopist for assistance in interpreting the minor bands. The spectroscopist looks at band shape as well as band location and, when possible, apportions a band to two structures if both could possibly contribute to that band and if the presence of both is indicated by other bands. Matching between component bands in the test spectra and reference spectra is done when possible.

The IR spectroscopist interprets a spectrum and then presents the results to the MS spectroscopist. These IR data, and especially information about functional groups, are useful to the spectroscopist in his interpretation efforts. After the MS spectroscopist interprets his spectrum, the two

spectroscopists meet again to deal with differences in results; for example, acids indicated by IR data but not by MS data.

The IR spectroscopist spends 30 to 45 minutes on complex spectra such as those that often result from LC5-LC7 fractions. Simple spectra such as those that often result from LC1 fractions can be interpreted in 5 minutes.

5.4.3.3 Contractor C

At "C," two individuals are involved in IR analysis. The first of these, a technical specialist with 10 years' experience, prepares the KBr pellets and obtains the spectra. The spectra are interpreted by a second person with 25 years of experience.

The approach taken by this spectroscopist is to first interpret the major IR peaks by memory. On the basis of these results and MS data, candidates for compounds present in the sample are decided upon. Reference spectra for these compounds are obtained from literature sources or from measurement. The reference spectra are compared to bands in the test spectrum. When positive matches are made, the bands in the test spectra that are apparently due to these compounds are checked off and attempts are then made to interpret the remaining bands. The IR and MS spectroscopists interact regularly during the course of analysis. Finally, the IR spectroscopist normally spends about 2 hours on the spectrum of an unknown. In this study, RTI indicated that all bands should be interpreted and all interpretations should be rationalized; subsequently the spectroscopist spent about 4 hours on each IR spectrum included in this study.

5.4.3.4 Contractor D

Two individuals are involved in IR analysis at "D." A technician with 25 years of experience makes the IR measurements. A second person with 11 years of experience carries out the interpretations. This spectroscopist makes about 80 percent of the band assignments on the basis of memory and 20 percent through the use of reference works; for example, the Sadtler tables and a text by L. J. Bellamy (1958). All bands, weak, medium, and small, in the $4000\text{--}1640\text{ cm}^{-1}$ range are interpreted but only medium and strong bands in the $1650\text{--}600\text{ cm}^{-1}$ range are interpreted. The spectroscopist normally spends about 15 minutes on normal Level 1 IR spectra but spent about 2 hours on each of the spectra included in this study. Finally, the IR and MS spectroscopists

interpret their spectra and then get together and decide what compounds and/or classes of compounds are indicated collectively by the spectra. The spectroscopist also commented on the quality of the test spectra:

In general the spectra were of excellent quality and not very representative of Level 1 LC fractions. If more time were available for interpretation, exact spectral matches could be made in most cases. The Level 1 forms (IERL-RTP Procedures Manual) are a waste of the time they take to completely fill out. The spectra themselves can be adequately labeled and reproduced in reports and the forms should be eliminated. The IR analysis report forms provided with this task were an improvement over the standard Level 1.

5.4.4 Summary and Argument for Computer Assistance

One will note that the level of experience of the IR spectroscopists varies from about 6 months to 25 years. Despite these differences in experience, the approaches taken by the spectroscopists are similar. Each depends, for the most part, on memory to make assignments, but each also makes use of reference works. It is noted that the "A" and "C" spectroscopists interact regularly with the mass spectroscopist during the interpretation process whereas the IR and mass spectroscopists at "B" and "D" compare and contrast results after they have completed their respective spectral interpretations. Finally, the time spent on the IR spectra varied from 1 hour to about 4 hours, though this 4 hours included time for assignment of essentially all the IR bands in the test spectra through matching with reference spectra.

The quality of the results presented by each spectroscopist is, in general, a reflection of his or her level of experience and the time given to interpretation of each spectrum, though the correlation is not strong. In fact, it is the thoroughness of the interpretation that seems to have the greatest bearing on the quality of the results. A thorough interpretation requires, however, that the spectroscopist consider all possible (and reasonable) structures that could be present in a sample. This means that the spectroscopist must have thorough training and/or a great deal of experience. Alternatively, he or she must make extensive use of reference materials. In either case, thoroughness may be expensive in terms of dollars and hours. Such thoroughness may also present a problem as the work load in the environmental assessment area increases.

In order to deal with both the need for thoroughness in interpretation and the increased work load, it is appropriate to consider the utilization

of some sort of computer assistance for the spectroscopist. A review of the pertinent literature, using mainly the review issues of Analytical Chemistry as the reference source, revealed that a number of attempts to use such mechanical interpretations have been made. The approaches are computerized techniques involving pattern recognition, artificial intelligence, or matching with a library of spectra. Of these, artificial intelligence seems to be the most appropriate for Level 1 samples where a spectrum is likely to represent a mixture of compounds. Briefly, this approach attempts to parallel human reasoning as much as possible when interpreting a spectrum. A set of rules for interpretation in terms of functional groups is developed and incorporated into a computer program. The spectrum to be interpreted is encoded in terms of frequency, intensity, and shape for each band and this information is examined by the computer using the decision rules to decide whether or not a given functional group is present. Obviously, the quality of this mechanical interpretation is primarily dependent on the set of decision rules used.

At the very least, a computer program that presents all possible, reasonable assignments of bands or groups of bands could be developed. The spectroscopist would then, on the basis of his or her experience, decide which assignment(s) would most likely be correct. The computer would replace the tables now used and would offer the advantage of making the spectroscopist aware of all possible assignments, several of which the spectroscopist would otherwise possibly fail to consider.

SECTION 6

RESULTS OF LRMS MEASUREMENT AND INTERPRETATION

6.1 INTERPRETATION OF TEST LRMS SPECTRA

6.1.1 Introduction

The spectral interpretation test results were evaluated by studying the completed reporting forms filled out by the contractors and by discussing the results with the mass spectroscopists who performed the analyses. Wherever possible, the interpretation based on LRMS was separated from that aided by IR. In certain cases, the IR and LRMS analysts worked together during the interpretation; thus, clear differentiation was not possible. The test spectra are shown in Figures 7 through 12. In evaluating the results it was soon apparent that very often a category assignment was itself based on assignment of peaks to one compound. Nevertheless, the primary goal of Level 1 environmental assessment is the identification of compound classes. Thus, for the purposes of this study, correct compound class identification is given greater significance than the identification of individual compounds or isomers of compounds although this information is also very important.

6.1.2 Overview of All Results

Synthetic mixtures LC4a and LC4b were five- and six-component mixtures, respectively, of compounds that fall in the Level 1 category of "fused alternate hydrocarbons, molecular weight less than 216." Correct category and intensity assignments for LC4a and LC4b (Table 34) were made by all contractors except for "B" who did not complete the Level 1 reporting forms as required. In general, there were no problem categories or compounds in LC4a and LC4b. As shown in Table 35, both mixtures contained naphthalene, anthracene, phenanthrene, 9-methyl anthracene, and 9,10-dimethyl anthracene and LC4b also contained 2,3-dimethyl naphthalene. The major difference in the two mixtures was that the anthracenes were the major components in LC4a and the naphthalenes were the major components in LC4b. All of the mixture

TABLE 34. CATEGORIES IN THE IR/LRMS SPECTRAL INTERPRETATION TEST CORRECTLY IDENTIFIED BY LRMS (SUM OF INTENSITIES OF COMPOUNDS IN THE CATEGORIES)

	Category	mg/L	Weight %	Contractor			
				A	B	C	D
LC4a	Fused alternate, nonalter- nate hydrocarbons	15,835	100.0	810	*	630	320
LC4b	Fused alternate, nonalter- nate hydrocarbons	16,813	100.0	260	*	280	321
LC5a	Fused alternate, nonalter- nate hydrocarbons	3,016	14.0	NR	NR	20	NR
	Heterocyclic nitrogen compounds	18,584	86.0	130	*	330	231
LC5b	Heterocyclic nitrogen compounds	12,105	92.2	210	*	340	110
	Ketones	1,016	7.7	110	*	10	111
LC6a	Heterocyclic nitrogen compound or phenol or ketone	4,214	67.9	100	NR	100	NR
	Phenol	1,992	32.1	30	NR	20	NR
LC6b	Ketone	2,074	22.6	NR	**($\frac{1}{2}$)	$\frac{1}{2}$	111
	Phenol	1,026	11.2	100	NR	NR	NR
	Ether or acid	2,066	22.5	NR	**($\frac{1}{2}$)	10	NR
	Ketone or acid	1,992	21.7	NR	*	100	**($\frac{1}{2}$)
	Acid	2,037	22.2	NR	*	10	NR
Total correct out of 13				8	8	11 $\frac{1}{2}$	6 $\frac{1}{2}$

NR = Not reported.

*Category identified but intensity not given. Category assignment made by RTI on the basis of contractors' data.

In each of these cases half credit was given:

**("C") category of ketone was identified but was based on 9-fluorene-4-carboxylic acid and not 9-fluorenone.
("D") Category of ketone identified by assignment was based on 9-fluorenone and not 9-fluorenone-4-carboxylic acid; ("B") acid category of ether or acid identified, but assignment was based on 9-fluorenone-4-carboxylic acid and not o-phenoxybenzoic acid. Also ketone category was identified but assignment was based on 9-fluorenone-4-carboxylic acid and not 9-fluorenone.

NOTE: Categories missed by all contractors: none.

TABLE 35. COMPOUNDS IN THE IR/LRMS SPECTRAL INTERPRETATION TEST CORRECTLY IDENTIFIED BY LRMS

	Compound	MW	mg/L	Weight %	Contractor			
					A	B	C	D
LC4a	Naphthalene	128	980	6.2	10	NR	10	10
	Anthracene	178	5,868	37.1	100	*	100	100
	9-Methyl anthracene	192	3,980	25.1	100	*	100	100
	Phenanthrene	178	980	6.2	100	*	100	100
	9,10-Dimethyl anthracene	206	4,027	25.4	100	*	100	10
LC4b	Naphthalene	128	5,880	35.0	10	NR	10	100
	Anthracene	178	3,920	23.3	100	*	100	100
	9-Methyl anthracene	192	986	5.9	10	*	10	100
	Phenanthrene	178	3,928	23.4	100	*	100	100
	9,10-Dimethyl anthracene	206	1,034	6.2	10	*	10	10
LC5a	2,3-Dimethyl naphthalene	156	1,065	6.3	10	NR	10	10
	Fluorene	166	1,964	9.1	NR	NR	NR	NR
	2,3-Benzofluorene	216	1,052	4.9	NR	NR	10	NR
	n-Ethyl carbazole	195	11,265	52.1	NR	NR	100	100
	2-Methyl indole	131	1,937	9.0	10	NR	10	10
LC5b	Carbazole	167	4,328	20.0	100	NR	100	100
	2,3-Dimethyl indole	145	1,054	4.9	10	NR	10	10
	7,8-Benzoquinoline	179	2,155	16.1	100	*†	100	100†
	Phenanthradine	179	4,002	30.5	100	*†	100	100†
	1,10-Phenanthroline	180	2,032	15.5	NR	NR	NR	NR
	Phenazine	180	3,956	30.2	NR	NR	100	NR
	Anthrone	194	1,016	7.7	NR	NR	NR	NR

(continued)

TABLE 35. (continued)

	Compound	MW	mg/L	Weight %	Contractor			
					A	B	C	D
LC6a	2-Hydroxy pyridine	95	4,214	67.9	100	NR	100	NR
	2,6-Dimethyl phenol	122	1,022	16.5	10	NR	10	NR
	6-6-Biphenol	186	970	15.6	10	NR	10	NR
LC6b	9-Fluorenone	180	2,074	22.6	NR	NR	NR	NR
	2,6-Dimethyl phenol	122	1,026	11.2	NR	NR	NR	NR
	o-Phenoxy benzoic acid	214	2,066	22.5	NR	NR	10	NR
	1-Fluorene carboxylic acid	210	2,037	22.2	NR	*	10	NR
	9-Fluorenone-4-carboxylic acid	224	1,992	21.7	NR	*	100	NR
Total correct out of 30					19	12	25	17

NR = Not reported.

*Compound was reported but intensity was not reported as required by Level 1.

†Credit was given for assignment of isomers of actual test spectra compounds. For example, assignment of ethyl anthracene was considered correct although dimethyl anthracene was the actual compound. Also, credit was given here for the assignment of acridine instead of 7,8-benzoquinoline and phenanthradine because all three are isomers and have nearly identical mass spectra.

NOTE: Compounds missed or incorrectly identified by all contractors: fluorene, 1,10-phenanthroline, anthrone, 9-fluorenone, and 2,6-dimethyl phenol.

compounds in LC4a and LC4b were correctly identified by all four contractors except for the naphthalenes, which were missed by "B". The intensity assignments for phenanthrene in LC4a and naphthalene in LC4b did not, in general, follow the expected trend; most contractors assigned the minor component phenanthrene a major component intensity and the major component naphthalene a minor component intensity.

Synthetic mixtures LC5a and LC5b were six- and five-component mixtures, respectively, containing primarily heterocyclic nitrogen compounds and lesser quantities of fused nonalternate hydrocarbons and ketones.

The fused alternate hydrocarbons in LC5a (fluorene and 2,3-benzofluorene) were, in general, not identified nor was the category assignment correctly made in three out of four cases. The heterocyclic nitrogen compounds in LC5a (n-ethyl carbazole, 2-methyl indole carbazole and -2,3-dimethyl indole) were, in general, correctly identified. The category assignment was also correctly made in most cases although the major component in LC5a, n-ethyl carbazole, was missed by two out of four contractors. The intensity assignments were generally correct.

The ketone (anthrone) in LC5b was missed by all contractors and, although all contractors reported the ketone category as present, the identification was, in all cases, based on an incorrect assignment. The category and intensity assignments for the heterocyclic nitrogen compounds in LC5b were, in general, correct. The heterocyclic nitrogen compounds in LC5b (7,8-benzoquinoline, phenanthradine, 1,10-phenanthroline, and phenazine) were, in general, not identified correctly. Phenanthroline was missed by all contractors and phenazine was identified correctly by only one contractor. Benzoquinoline and phenanthradine, which are isomers essentially indistinguishable by LRMS, were either identified by name or as another isomer of these two isomers, acridine, by three out of four contractors.

Synthetic mixtures LC6a and LC6b were three- and five-component mixtures containing acids, ketones, phenols, and several compounds containing combinations of these functional groups. Two out of the four contractors identified all three categories and compounds correctly and at the proper intensities; however, the other two contractors did not identify any of the correct categories and compounds. The major component of LC6a, 2-hydroxy pyridine, was identified by several contractors as 2-pyridone. Either designation is correct because the compound tautomerizes easily.

Mixture spectrum LC6b was, by far, the most difficult for the contractors to interpret. In general, ketones, acids, and phenols were not identified correctly. Half credit was given for correct category identification if the identification was based on the wrong compound (see the explanations at the end of Table 34). This applies only to spectrum LC6b. Only two of the five compounds were identified by two out of the four contractors. Fluorenone and 2,6-dimethyl phenol were not identified by any contractors and o-phenoxy benzoic acid was identified by only one contractor.

Of the five compounds missed by all contractors, only two--9-fluorenone and 2,6-dimethyl phenol in LC6b--had molecular ions that were less than 10 percent of the maximum based on single ion plots (see Table 22). Thus, the categories and compounds most often missed were probably missed due to interpretation problems and not to the quality of the spectra themselves, although several contractors did state that their interpretations were handicapped by the availability of only a single spectrum for each fraction.

Overall, "C" and "A" were more successful in identifying individual compounds than "D" and "B"; "C" was more successful than the other three in identifying categories.

To distinguish differences in how contractors interpreted the test spectra, two specific elements of the interpretation were examined. In Table 36, the contractors' LRMS signal assignments for the molecular ions in the spectra were compared. In Table 37, all of the ions (molecular and fragment) assigned by the contractors to the compounds they correctly identified were compared. Finally, in Table 38, those compounds reported that were not known to be present in the spectra were compared along with the compounds or fragments for which these compounds were most likely mistaken. In general, five types of errors were suggested by these tables. Errors of omission--not noting the presence of molecular ions--were primarily a problem for "B", as shown in Table 35, and for the contractors in general in LC6b. Obviously, then, finding the molecular ion is an important step in the interpretation/identification process. Reporting molecular ions as fragment ions and vice versa was another significant error. For example, fluorene in LC5a (Table 36) was not correctly identified by any contractor, but two contractors reported the molecular ion as a fragment ion for carbazole, which it also is. In the case of fluorene, the mistake is understandable because many of the eight most abundant ions, including the molecular

TABLE 36. CONTRACTORS' LIMS SIGNAL ASSIGNMENTS FOR SPECIFIC MOLECULAR IONS IN THE LRMS TEST SPECTRA

Fraction	Ion	Expected	Contractor			
			A	B	C	D
LC4a	128	Naphthalene	Naphthalene	NA	Naphthalene	Naphthalene
	178	Anthracene, phenanthrene	Anthracene, phenanthrene	Anthracene, phenanthrene	Anthracene or phenanthrene	Anthracene or isomer
	192	9-Methyl anthracene	Methyl anthracene or methyl phenanthrene	Methyl anthracene	Methyl anthracene or methyl phenanthrene	Methyl anthracene or isomer
	206	9,10-Dimethyl anthracene	Dimethyl anthracene or phenanthrene	Dimethyl- or ethyl anthracene or phenanthrene	Dimethyl anthracene or dimethyl phenanthrene	Ethyl anthracene or isomer
LC4b	128	Naphthalene	Naphthalene	NA	Naphthalene	Naphthalene
	178	Anthracene, phenanthrene	Anthracene, phenanthrene	Anthracene, phenanthrene	Anthracene or phenanthrene	Anthracene or isomer
	192	9-Methyl anthracene	Methyl anthracene or phenanthrene	Methyl anthracene	Methyl anthracene or phenanthrene	Methyl anthracene or isomer
	206	9,10-Dimethyl anthracene	Dimethyl anthracene or phenanthrene	Dimethyl- or ethyl anthracene or phenanthrene	Ethyl anthracene or dimethyl anthracene or dimethyl phenanthrene	Ethyl anthracene or isomer
LC5a	156	2,3-Dimethyl naphthalene	Dimethyl naphthalene	NA	Dimethyl naphthalene	Dimethyl naphthalene
	166	Fluorene	Fragment of phenanthridone, carbazole, methyl carbazole, unidentified	NA	Fragment of carbazole, ethyl carbazole, or dimethyl carbazole	NA
	216	2,3-Benzofluorene	Unidentified	NA	Methyl pyrene or benzo-fluorene	NA
	195	n-Ethyl carbazole	Phenanthridone, acridone	Acridone	Ethyl carbazole or dimethyl carbazole	Ethyl carbazole
	131	2-Methyl indole	Methyl indole	NA	Methylindole	Methyl indole
	167	Carbazole	Carbazole	Acridone fragment ion	Carbazole	Carbazole
145		2,3-Dimethyl indole	Dimethyl indole	NA	Dimethylindole	Ethyl indole

(continued)

TABLE 36. (continued)

Fraction	Ion	Expected	Contractor			
			A	B	C	D
LC5b	179	7,8-Benzquinoline, phenanthridine	Benzoquinoline, phen- anthridine	Acridine	7,8-Benzquinoline or phenanthridine	Acridine
	180	1,10-Phenanthroline; phenazine	Fluorenone	Fluorenone	Phenazine, fragment of anthraquinone or dimethyl benzol[c]cin- noline	Fluorenone
	194	Anthrone	Methyl fluorenone	Methyl fluorenone	Methyl benzoquinoline or methyl benzol[c]- cinnoline	Methyl fluorenone
LC6a	95	2-Hydroxy pyridine	Hydroxy pyridine	NA	2-Pyridone	Phenyl ether fragment
	122	2,6-Dimethyl phenol	Cresol, ethyl phenol	NA	Dimethyl phenol	Phenyl ether fragment
	186	6-6-Biphenol	Biphenyldiol (6-6-biphenol)	NA	6-6-Biphenol	Phenyl ether
LC6b	180	9-Fluorenone	NA	NA	NA	NA
	122	2,6-Dimethyl phenol	NA	NA	o-Phenoxy benzoic acid fragment	NA
	214	o-Phenoxy benzoic acid	NA	NA	o-phenoxy benzoic acid	NA
	210	1-Fluorene carboxylic acid	NA	Carboxy fluorene	Fluorene carboxylic acid	Methyl xanthone
	224	9-Fluorenone-4-carbox- ylic acid	Hydroxyanthraquinone	Carboxy fluorenone or carboxy methyl fluo- rene	9-Fluorenone-4-carbox- ylic acid	Dimethyl or ethyl xanthone

NA = Not assigned.

TABLE 37. LRMS SIGNAL ASSIGNMENTS FOR COMPOUNDS IN THE SPECTRAL INTERPRETATION TEST SPECTRA

	Compound	MW	Weight %	Contractor			
				A	B	C	D
LC4a	Naphthalene	128	6.2	128	NR	128, 127, 129, 64, 51, 126, 102, 63	128
	Anthracene	178	37.1	178, 179, 176, 89, 152, 151, 150, 177	178	178, 176, 179, 89, 76, 88, 151, 152	178
	9-Methyl anthracene	192	25.1	192, 191, 189, 193, 94.5	192, 206, 191	192, 191, 189, 193, 94.5, 96, 82.5, 190	192
	Phenanthrene	178	6.2	178, 179, 176, 89, 152, 151, 150, 177	178	178, 176, 179, 89, 76, 88, 151, 152	178
	9,10-Dimethyl anthracene	206	25.4	206, 191, 205, 207, 189, 165, 202, 203, 204	192, 206, 191	206, 191, 207, 189, 89, 192, 101, 82.5	206
LC4b	Naphthalene	128	35.0	128	NR	128, 127, 129, 64, 51, 126, 102, 63	128
	Anthracene	178	23.3	178, 179, 176, 89, 152, 151, 150	178	178, 179, 176, 89, 177, 152, 151, 76	178
	9-Methyl anthracene	192	5.9	192, 191, 189, 193, 94.5	192, 206	192, 191, 189, 193, 94.5, 96, 82.5, 190	192
	Phenanthrene	178	23.4	178, 179, 176, 89, 152, 151, 150, 177	178	178, 179, 176, 89, 177, 152, 151, 76	178
	9,10-Dimethyl anthracene	206	6.2	206, 191, 205, 189, 202, 203, 204, 207, 165	192, 206	206, 191, 207, 189, 89, 192, 101, 82.5	206
	2,3-Dimethyl naphthalene	156	6.3	156, 141	NR	156, 141, 155, 115, 157, 142, 76, 153	156
LC5a	Fluorene	166	9.1	NR	NR	NR	NR
	2,3-Benzofluorene	216	4.9	NR	NR	216, 215, 94.5, 217, 108, 213, 202, 107.5	NR

(continued)

TABLE 37. (continued)

Compound	MW	Weight %	Contractor			
			A	B	C	D ^a
LC5a (con.)	195	52.1	NR	NR	180, 195, 152, 166, 140, 139, 151, 196	195
	131	9.0	130, 131	NR	130, 131, 65, 77, 51, 103, 78, 102	131
	167	20.0	167, 166, 139	NR	167, 166, 168, 83.5, 179, 63, 69.5	167
	145	4.9	144, 145	NR	144, 145, 130, 143, 77, 115, 146, 103	145
	179	16.1	179, 150, 151, 152, 153	NR	179, 178, 180, 89.5, 151, 76, 89, 152	NR
LC5b	179	30.5	179, 150, 151, 152, 153	NR	179, 178, 180, 89.5, 151, 76, 89, 152	NR
	180	15.5	NR	NR	NR	NR
	180	30.2	NR	NR	180, 179, 90, 76, 153, 128, 63, 154	NR
	194	7.7	NR	NR	NR	NR
	95	67.9	95, 67, 41, 51	NR	95, 67, 41, 66	NR
LC6a	122	16.5	122, 107, 77, 51	NR	122, 107, 121, 77, 51, 79, 91	NR
	186	15.6	186, 157, 158, 131, 139, 128, 129, 127	NR	186, 157, 158, 131 187, 139, 128, 185	NR
	180	22.6	NR	NR	NR	NR
	122	11.2	NR	NR	NR	NR
	214	22.5	NR	NR	121, 214, 51, 77, 65, 120, 122	NR
9-Fluorene 2,6-Dimethyl phenol 0-Phenoxybenzoic acid	210	22.2	NR	210, 165	165, 210, 166	NR
	224	21.7	NR	224, 179	224, 225, 207, 151, 179, 152, 139	NR

^a D^a listed fragment ions for all compounds reported. Thus, the corresponding fragments could not be differentiated.

TABLE 38. COMPOUNDS REPORTED THAT WERE NOT INCLUDED IN THE TEST SPECTRA
(OTHER THAN METHYL/ETHYL ISOMERS OF THE EXPECTED COMPOUNDS)

Contractor	Compound	LC fraction	LRMS intensity	MW	Mistaken for
A	Unidentified	4b	1	184	Unknown
	Unidentified	4b	1	211	Unknown
	Fluorenone	5a	100	180	N-ethyl carbazole fragment
	Phenanthridine	5a	100	195	N-ethyl carbazole
	Acridone	5a	100	195	N-ethyl carbazole
	Methyl carbazole	5a	10	181	Unknown
	Methyl pyrene	5a	10	215, 216	2,3-Benzofluorene
	Unidentified	5a	1	202	2,3-Benzofluorene fragment
	Unidentified	5a	1	209	Unknown
	Unidentified	5a	1	230	Unknown
	Fluorenone	5b	100	180	1,10-Phenanthroline or phenazine
	Alkyl phenanthradines	5b	10	193-207	Unknown
	Alkylfluorenones	5b	10	194-208	Unknown
	Cresol	6a	10	122 (wrong MW)	2,6-Dimethylphenol
	Unidentified	6a	10	168	Unknown
	Unidentified	6a	10	169	Unknown
	Unidentified	6a	10	179	Unknown
	Unidentified	6a	10	180	Unknown
	Unidentified	6a	10	195	Unknown
	Hydroxyanthraquinone	6b	100	224	9-Fluorenone-4-carboxylic acid
	Unidentified	6b	100	120-139	Unknown
B	Acridone	5a	Not given	195	N-ethyl carbazole
	Fluorenone	5a	Not given	180	N-ethyl carbazole fragment
	Acridine	5b	Not given	179	7,8-Benzoquinoline or phenanthradine
	Methyl acridine	5b	Not given	193	Anthrone fragment
	Dimethyl acridine	5b	Not given	207	Unknown
	Ethyl acridine	5b	Not given	207	Unknown
	Fluorenone	5b	Not given	180	1,10-Phenanthroline or phenazine

(continued)

TABLE 38. (continued)

Contractor	Compound	LC fraction	LRMS intensity	MW	Mistaken for
B (continued)	Methyl fluorenone	5b	Not given	Not given	Unknown
	Dimethyl fluorenone	5b	Not given	Not given	Unknown
	Ethyl fluorenone	5b	Not given	Not given	Unknown
	Carboxymethylfluorene	6b	Not given	224	9-Fluorenone-4-carboxylic acid
C	Pyrene	4a	10	202	Unknown
	Fluoranthene	4a	10	202	Unknown
	Unidentified	4a	1	238	Unknown
	Unidentified	4a	1	224	Unknown
	Unidentified	4b	1	202	Unknown
	Unidentified	4b	1	209	Unknown
	Methyl carbazole	5a	10	181	Unknown
	Methyl pyrene	5a	10	216	Unknown
	Unidentified	5a	1	209	Unknown
	Unidentified	5a	1	230	Unknown
	Methyl benzo[h]quinoline	5b	10	193	Anthrone fragment
	Methyl benzo[c]cinoline	5b	10	194	Anthrone
	Dimethyl benzoquinoline	5b	10	207	Unknown
	Anthraquinone	5b	10	208	Unknown
	Dimethyl benzo[c]cinoline	5b	10	208	Unknown
	Unidentified	6a	1	195	Unknown
	Unidentified	6a	1	180	Unknown
	Unidentified	6a	1	179	Unknown
	Unidentified	6b	1	239	Unknown
D	Pyrene	4a	10	202	Unknown
	Acenaphthene	4a	10	152	Anthracene, phenanthrene fragment
	Acridine	4b	100	179	Anthracene, phenanthrene fragment
	Acenaphthene	4b	100	152	Anthracene, phenanthrene fragment
	C ₄ -branched naphthalene	4b	1	184	Unknown

(continued)

TABLE 38. (continued)

Contractor	Compound	LC fraction	LRMS intensity	MW	Mistaken for
D (continued)	Methyl carbazole	5a	10	181	Unknown
	Propyl carbazole	5a	1	209	Unknown
	Acridine	5b	100	179	7,8-Benzoquinoline or phenanthradine
	Fluorenone	5b	100	180	1,10-Phenanthroline or phenazine
	N-ethyl acridine	5b	10	193	Anthrone fragment
	Methyl fluorenone	5b	10	194	Anthrone
	Chalcone	5b	1	208	Unknown
	Phenyl ether (OH)	6a	100	186	Diphenol
	C ₂ -xanthone	6b	100	224	9-Fluorenone-4-carboxylic acid
	C ₁ -xanthone	6b	10	210	1-Fluorene carboxylic acid
	Xanthone	6b	1	196	Unknown
	Unassigned		Not given	216, 230	Unknown

NOTES: Compounds reported by all contractors: none

Compounds reported by three out of four contractors: Methyl carbazole in 5a
Fluorenone in 5b
Methyl fluorenone in 5bCompounds reported by two out of four contractors: Pyrene in 4a
Fluorenone in 5a
Acridine in 4b (D), 5b (A)

ion, were also fragment ions of the more dominant components, carbazole and n-ethyl carbazole. In LC5a (Table 38), Contractors A and B incorrectly identified the mass 180 fragment ion for n-ethyl carbazole as fluorenone. In several cases the molecular ion was simply identified incorrectly as belonging to another compound. Contractors A and B identified n-ethyl carbazole in LC5a as acridone (Table 38). The final kind of error observed was the "homolog error," or finding a molecular ion for one compound and then, based on this identification, mistakenly identifying other molecular ions as homologs of the first. Contractors B and D made this error in identifying the molecular ion 180 in LC5b incorrectly as fluorenone and then incorrectly identifying anthrone as methyl fluorenone (Table 38).

Table 37 shows the disparity in the use of the spectral data. "A" and "C" generally reported the eight most abundant peaks for the compounds they identified. How many of these were obtained directly from the spectra and how many were simply matched against tabulated reference spectra after one or more characteristic peaks were identified is not important in this discussion, but will be addressed later. The important point is that these contractors used many peaks to identify categories/compounds. Contractor B generally reported only molecular ions. Contractor D lumped all fragment ions together so that fragment ions for one compound could not be distinguished. The results indicate that thoroughness of the interpretation is correlated with the success of the interpretation.

6.1.3 Results and Comments From Specific Contractors

6.1.3.1 Contractor A Test Spectra Results and Comments--

Contractor A correctly identified 8 out of 13 categories in the test spectra. All categories were correctly identified in LC4a, LC4b, LC5b, and LC6a. Of the five categories incorrectly identified by "A", three were missed by three out of four contractors, and the rest by two out of four contractors. Again, as was the case for the contractors in general, acids and ketones were problem categories for "A". Contractor A correctly identified 19 out of 30 compounds in the test spectra. All compounds in LC4a, LC4b, and LC6a were correctly identified. Most of the incorrect compound assignments were in LC5b and LC6b. Of the 11 compounds missed by "A", 5 were missed by all contractors, and 3 more by 3 out of 4 contractors. The LRMS

data interpretation was made completely independently of the IR interpretations.

The category assignment of fused alternate, nonalternate hydrocarbons MW <216 for LC4a is correct according to Table 17, page 154, of the Level 1 manual. In the interpretation of spectrum LC4a, all peaks above m/e 110 and greater than 10 percent intensity were accounted for by the identifications. The assignment rationale was that reference spectra of the three major components identified, combined in appropriate amounts, were a good match for the supplied spectrum. These "three" major components were listed on the Level 1 LRMS report form as anthracene/phenanthrene, methylanthracene/phenanthrene, and dimethyl/ethyl anthracene/phenanthrene, with naphthalene as a minor component. This acknowledges that although all of the expected mixture components were reported, the isomers of anthracene and phenanthrene and methylated anthracene homologs could not be distinguished by LRMS nor could ring substitution positions be specified. This is, of course, not unexpected. The signal assignments for each compound identified consisted of five to eight peaks except for naphthalene, where only the molecular ion, 128, was given. These signal assignments give two clues to the interpretive process. First, the reference "spectra" used contain many of the peaks for the test compounds. Second, molecular ions for certain compounds are easily recognizable even in a mixture in which the fragment ions are very weak. In the case of naphthalene, none of the eight most abundant peaks above m/e 110 were of greater than 10 percent intensity and only two of the eight (51 and 63), other than 128, were of greater than 10 percent intensity.

The category assignment for LC4b was fused alternate, nonalternate hydrocarbons, intensity 100, MW 128-206. Although this is correct, there is no apparent reason why the MW range given here should be different from that listed in LC4a. In the interpretation of spectrum LC4b, all peaks above m/e 120 and greater than 10 percent intensity were included in the analysis. This included two very weak (<10 percent) unidentified peaks at 184 and 211 that could not be attributed to any of the mixture compounds. There is an actual peak at 184, but there is no peak at 211. The peak mentioned is probably at 209. The assignment rationale was similar to that for LC4a. It was assumed by "A" that because the m/e 178 ion in the spectrum appeared (based on the m/e peaks at 176, 177, and 179) to be saturated by 5X, the

major part of the rest of the spectrum was readily correlated to anthracene/phenanthrene and the associated homologs. According to the intensity ratios for pure anthracene/phenanthrene and for the mixture peaks as given in Table 24, though, the saturation of 178 is probably closer to 3-4X. The identified components were listed in the LRMS report as anthracene/phenanthrene, naphthalene, dimethyl naphthalene, methyl anthracene/phenanthrene, and dimethyl anthracene/phenanthrene with anthracene/phenanthrene the major components and the rest minor. The most obvious reason why naphthalene at 35 percent of the mixture by weight and the major component of mixture LC4b was assigned a 10 percent intensity in the LRMS report is that the naphthalene molecular and fragment ions are just not as intense as the anthracene/phenanthrene group ions. However, it is also likely that some naphthalene was lost into the vacuum of the mass spectrometer operated in the direct probe inlet mode. A quantitatively accurate representation of naphthalene in LC4b would probably have required that the spectrum be taken with the mass spectrometer operated in the batch inlet mode. The naphthalene molecular ion was present at 36 percent intensity, essentially the same as for the minor components, dimethyl anthracene and methyl anthracene. Also, none of the naphthalene fragment ions greater than m/e 120 were greater than 10 percent intensity. Clearly an accurate semiquantitative estimate of naphthalene in spectrum LC4b cannot be made on the basis of LRMS alone. The signal assignments were also nearly the same as for LC4b. The new compound in LC4b, dimethyl naphthalene, was identified on the basis of two peaks, the molecular ion at 156 and a fragment ion at 141. Again, as was the case with naphthalene in both LC4a and LC4b, these two peaks were the only two of the eight most abundant that met "A's" intensity-m/e range criteria. In the interpretation of spectrum LC5a, all m/e values greater than 10 percent intensity above m/e 120 were assigned. In addition, many other ions below m/e 120 were assigned. The assignment rationale was to match prominent peaks to reference spectra and thereby make as complete an accounting of the spectrum as possible. A tolerance of ± 1 LC fraction from the expected (page 154, Level 1 manual) was used in considering possible compounds. Saturated peaks (100 percent intensity) such as m/e 180 and 195 prevented the accurate evaluation of whether the $M \pm 1$ peaks were isotopes or separate species. It was assumed by "A" that, in this case, m/e 181 was a separate species and m/e 196 was an isotope (C^{13}) of 195. For these two peaks, the

assumption made was valid according to Table 24. On the Level 1 report form, methyl indole, dimethyl indole, and carbazole were correctly listed as components of the mixture. The indoles were correctly listed as minor components and carbazole was listed as a major component. Three other compounds were listed that were not included in the mixture. Fluorenone (m/e 180) and phenanthridone/acridinone (m/e 195) were listed as major components and methyl carbazole (m/e 181) was listed as a minor component. Finally, peaks at 215 and 216 were listed as unidentified minor components. Although they were originally attributed to methyl pyrene (MW 216), this was discounted because the LC fraction (5) was outside the ± 1 LC fraction tolerance set by "A". Methyl carbazole is probably an impurity in the carbazole and ethyl carbazole and was also reported at 10 percent intensity by "C" and "D". Fluorenone, also reported by "B", has at least six of the eight most abundant peaks in the spectrum. The "fluorenone" molecular ion is actually a major fragment ion of ethyl carbazole and the reported fragment ions for fluorenone are most likely due to carbazole and ethyl carbazole. The assignment of m/e 195 to phenanthridone/acridinone (acridone) was also made by "B". The peaks listed by "A" for acridone are among the eight most abundant for acridone. The molecular ion 195, however, actually corresponds to ethyl carbazole and the fragment ion to ethyl carbazole, carbazole, and fluorene. The peaks at 216 and 215 originally listed as methyl pyrene are the molecular and major fragment ion for 2,3-benzofluorene. However, these two ions are the same for methyl pyrene and benzofluorene. "C" also assigned methyl pyrene to m/e 216. The category assignment made in the LRMS report of heterocyclic-nitrogen compounds, intensity 100, MW range 181, was correct, although the MW range should actually be 131-195. Ketones were assigned intensity 100, MW range 180-195, due to the incorrect assignment for ethyl carbazole. The category fused alternate hydrocarbons (14 percent by weight) was not listed although methyl pyrene was originally listed. The signal assignments made varied from reporting only the molecular ion and/or a single fragment ion, methyl and dimethyl indole, to reporting several fragments along with the molecular ion. Two important pieces of information are gained from "A's" LC5a interpretation. Again, it is possible to identify some compounds solely by the molecular ion. Although the presence of a compound(s) in a mixture can be justified by matching mixture peaks to

reference spectra or lists of peaks, this does not guarantee that the compound or category is actually present in the mixture. Comparing intensity rates of peaks is also made more difficult when one or more peaks are saturated and also contribute to the spectrum of more than a single compound.

The category assignment for LC5b of heterocyclic nitrogen compounds, intensity 100, MW 179-200, was correct. Ketones were listed as being present although the MW range, 180-208, and intensity given were not correct due to the listing of fluorenone at 100 percent intensity as a mixture component. In the interpretation of spectrum LC5b, all peaks of greater than 10 percent intensity were included in the analysis. The assignment rationale was that although the two principal peaks, m/e 179 and 180, were both saturated in the spectrum, the apparently alkylated peaks at 193/194 and 207/208 show very similar ratios to each other. Therefore, it was assumed that 179/180 had a similar ratio also. The peaks above m/e 190 showed a commonly observed amount of alkylation to the nucleus. Identification was then made on the basis of comparison to reference spectra and separate species combined (summed) in the observed ratio. The LRMS report correctly listed both benzoquinoline and phenanthradine as major components. Fluorenone was listed at m/e 180 as a major component instead of the actual compounds contributing to 180, 1,10-phenanthroline, and phenazine. Anthrone, a minor component of the mixture was not listed but its molecular ion was included in the assignment of alkyl phenanthridine and alkyl fluorenones as minor components. The major fluorenone peaks were present in LC5b. Fluorenone and methyl fluorenone were also listed by "B" and "D". Contractor A's assignment of the alkylated fluorenone and phenanthradine homologs could not be verified due to unavailability of reference spectra. Only the molecular ions were listed for these compounds while several ions were listed by "A" for the suspected parent compounds, phenanthradine and fluorenone. In the interpretation of LC5b, then, all of the molecular ions were found but the compound assignments were not always correctly made probably due to insufficient information being available.

In the interpretation of spectrum LC6a, all peaks greater than 10 percent intensity and all peaks greater than 5 percent intensity above m/e 100 were considered. The assignment rationale was that m/e values as shown in signal assignments were satisfactory matches to reference spectra for those

compounds identified without missing or conflicting peaks. A number of small peaks at m/e 102, 113, 168, 169, 179, 180, and 195 were too small to identify without additional mass spectra taken at other temperatures and at 10 eV ionizing voltage. Note that these small peaks were not among the eight most abundant for the three-mixture components. In the LRMS report, "A" correctly identified all three components with respect to the intensity, composition, MW range, category, and assignment. Cresol and ethyl phenol were both listed as being present although 2,6-dimethyl phenol was actually in the mixture. However, the correct MW for cresol is 108, not 122. Ethyl and dimethyl phenols are probably indistinguishable in mixtures by LRMS. At least four peaks for each compound were listed.

In the interpretation of spectrum LC6b, all peaks above m/e 100 and 10 percent intensity were considered. The assignment rationale was that, except for one compound, it was not possible to separate out species adequately for identification without additional spectra taken at other temperatures and at 10 eV ionizing voltages.

The phenols category was reported but was based on the incorrect assignment of m/e 224 to hydroxyanthraquinone. The analyst did note that there were probably additional identified species from m/e 120 to m/e 239 and he marked a number of the molecular ions and prominent fragments on the spectra. An attempt was made to correlate several peaks (151, 165, 179) as part of a homologous alkylated series by assuming the loss of CH_2 groups to be responsible for the correlation. None of the expected compounds were identified correctly in LC6b.

In conclusion, several general techniques used by the "A" analyst were disclosed by the results of the spectral interpretation test.

1. The analyst marks peaks on the spectrum itself.
2. The intensities and mass range of the peaks to be studied are defined by a criterion to avoid having to interpret all peaks in a spectrum. In general, all peaks greater than m/e 100 and 10 percent intensity were interpreted with some peaks outside this range used when necessary.
3. Observed peaks thought to belong to one molecular ion are compared to a "reference spectrum" of the proposed compound.
4. When possible, attempts are made to correlate patterns of peaks as part of a homologous (usually alkylated) series and/or by comparing the intensity ratios of certain mixture peaks to those for a pure compound. Finally, the general

pattern of results suggested that dimethyl and ethyl isomers could not be distinguished nor could ring substitution positions be specified.

In general, the analyst did an adequate job of interpreting the spectra and a very good job of explaining the rationale for the interpretation.

The contractor made several comments about the choice of compounds used to make the mixture and the completeness of the information contained in the spectra. Contractor A stated that the use of relatively "simple" synthetic samples like LC4a-LC6b can actually complicate the interpretation of Level 1 organic spectra because several primary inputs to the analysis are missing. "A" pointed out that, in a real Level 1 analysis, the nature of the environment from which the sample is collected gives substantial clues as to the range of materials that may plausibly be present. This information gives the analyst a starting point for making first-round identification of spectral peaks and patterns, especially of major features. These intelligent first guesses are then retained, revised, or discarded in an iterative process of spectral interpretation that continues until all or virtually all spectral features are accounted for. In the iteration process the analyst relies on identifications from LC fractions adjacent to the one being analyzed because the LC fractionation system constitutes a continuum of one real sample. The pieces are more identifiable as parts of a whole than in isolation. For example, if one suspects phenols in a given LC5 fraction, one looks immediately at the corresponding LC6. The phenols, if that is what they are, will be more abundant in LC6 than in LC5. This kind of information confirms the LC5 identification. Also, real samples frequently contain homologous series of compounds. When any one member of the series is identified, it becomes easier to pick out the other.

The "A" analyst also pointed out that the LRMS spectra provided omitted a considerable amount of spectral information that is available from the LRMS that the analyst believes is needed for analysis of the spectra. If some LRMS labs are working without all of the necessary information, this may account for much of the perceived difficulty in interpretation. The Level 1 procedures manual does specify both probe temperature programming and use of several ionizing voltages, unless the spectra are so simple they can be readily interpreted.

Probe Spectra: Accurate representation of a sample by a single mass spectrum is essentially impossible unless the spectrum is synthesized from many. The reason is that sample vaporization is a dynamic process--the high-vapor-pressure materials will come off quickly at low temperature as soon as the sample is inserted, and will be completely vaporized and pumped away before the probe gets hot enough to vaporize the lower-vapor-pressure materials. Consequently, several spectra must be taken, spaced to cover the entire temperature range needed for sample vaporization. They must be complete spectra for each significant change in temperature. These several spectra not only more adequately represent the sample than is possible in a single spectrum, but have an additional feature of primary importance to species identification: they show the LC fraction in a thermally fractionated fashion, with significant species differentiation. This makes specific species or class assignments much more feasible than is possible from a composite spectrum.

Ionizing Voltage: When possible, spectra at each significant change in temperature should be run at both 70 eV and a low ionizing voltage, for example, 15 eV. The low ionizing voltage spectrum facilitates the recognition of individual compounds within the mix. The 70 eV spectra then provide spectra that can be matched against the reference literature. The difference between the two spectra provides important additional information needed for both specific and compound class identification.

RTI is in general agreement with "A" regarding the difficulty in adequately modeling a Level 1 organic sample by a simple synthetic mixture and a Level 1 low resolution mass spectrum by a single scan of this mixture. However, it has been RTI's experience that as a first attempt at studying a system like the Level 1 IR/LRMS scheme, much valuable information can be gained from analyses of simple round-robin samples and, although in some cases valuable inputs may be omitted, the significance of these inputs will be manifested in the contractor's results and comments. The problem with "real" environmental samples is that the composition and homogeneity of the sample is often unknown. Thus, there is seldom any reliable baseline data from which expected results can be derived. Real samples have a place in interlaboratory studies and are the desired kind of sample for evaluating interlaboratory precision, but synthetic samples offer the most reliable means of quickly characterizing a system.

6.1.3.2 Contractor B Test Spectra Results and Comments--

Contractor B correctly identified 8 out of 13 categories and 10 out of 30 compounds in the test spectra. All categories in LC4a, LC4b, and LC5b were correctly identified. All compounds in LC4a and LC4b except the naph-

thalenes were correctly identified. Of the six categories missed by "B", three were missed by three out of four contractors. The problem categories for "B" were, in general, acids, ketones, and phenols in LC6a and LC6b. Most of the incorrect compound assignments were in LC5a, LC5b, LC6a, and LC6b. Out of the 19 compounds missed by "B", 5 were missed by all contractors and 3 were missed by three out of four contractors. Six compounds were missed only by "B"--the naphthalenes in LC4a and LC4b and carbazole and the indoles in LC5a. The LRMS interpretation was made independently of the IR interpretation although later a composite set of results was reported based on both interpretations.

A comprehensive evaluation of "B's" interpretation of the test spectra is not possible because the contractor did not complete the Level 1 LRMS report forms as requested and often did not provide a clear indication of the assignment rationale on the LRMS analysis forms provided. The contractor stated that the Level 1 forms were not completed because the forms were of little value due to the nature of the samples and because it was easier to show differences among various interpretations by tables instead of by forms. No relative intensities were assigned to the compounds identified. An additional table was constructed showing the compounds the analyst identified by LRMS prior to seeing the IR results, but the information is essentially the same as that presented in the LRMS analysis form.

The category assignment for LC4a was listed as fused aromatic hydrocarbons. In the interpretation of spectrum LC4a, the molecular ions for phenanthrene/anthracene and methyl/dimethyl anthracene/phenanthrene were listed. As expected, none of the isomers could be distinguished although "B" correctly listed the possibilities in each case. Peak 191 was listed, apparently to show the loss of CH_3 from dimethyl anthracene. The molecular ion for naphthalene was not listed. An attempt was made to quantitate each identified mixture compound although it is not clear how this was done and, in most cases, the quantitation was incorrect by a factor of 2.

In the interpretation of LC4b, similar results were observed with all compounds except the two naphthalenes listed. Molecular ions were again listed for the identified compounds and an attempt was again made to quantitate each component. Although this approach was again unsuccessful, "B" did correctly note that the basic difference between LC4a and LC4b is in the percentage of each component present.

There was no category assignment made for LC5a by "B" although the compounds listed by "B" corresponded to ketones (not present in LC5a) and heterocyclic nitrogen compounds (present in LC5a). In the interpretation of LC5a, none of the compounds were correctly identified. Acridone (m/e 195) and fluorenone (m/e 180) were listed along with "minor" amounts of higher molecular weight species not containing nitrogen. Acridone and fluorenone were most probably mistaken for n-ethyl carbazole molecular and fragment ions. Contractor B listed the finding of peak 167 due to loss of CO from 195 as the rationale for reporting acridone. After seeing the IR results, these interpretations changed.

In the interpretation of LC5b, acridine (m/e 179), an isomer of two of the mixture components, phenanthradine and 7,9-benzoquinoline, was listed. Also listed were small amounts of mono and dimethyl or ethyl fluorenone (m/e not given). The interpretations by Contractors A and D were similar. Although the molecular ions in most cases were not identified correctly, the quantitation of these ions was very good. Compounds in LC5b contributing to m/e 176 represented 46.6 percent of the mixture. Contractor B reported acridine (m/e 179) as 47 percent of the mixture. Similarly, the compounds contributing to m/e 180 represented 45.7 percent of the mixture. Contractor B reported fluorenone (m/e 180) as 47 percent of the mixture.

Spectrum LC6a could not be interpreted by "B" prior to seeing the IR results, although the molecular ions for two of the components, 2-hydroxy pyridine and o-o'-biphenol, were listed along with a 2-hydroxy pyridine fragment ion.

The category assignment given for LC6b was that of a fused aromatic carboxylic acid. Contractor B identified 1-fluorene-carboxylic acid (m/e 210) and 9-fluorenone-4-carboxylic acid (m/e 224) in LC6b on the basis of the molecular ions and the presence of peaks at 165 and 179 corresponding to the loss of carboxylic acid groups from both molecules. On the basis of the two compounds identified, "B" correctly noted that they were present in almost equal concentrations.

These results, though incomplete, do suggest several common approaches used by "B" to interpret the test spectra in general:

1. Only intense high-mass ions were studied.
2. Some indication was given that in several cases attempts were made to correlate fragments with molecular ions.

Contractor B also commented on the types of samples and spectra used in this study, stating that the samples were not complex enough to be representative Level 1 samples because individual compounds were identified in several cases. It had been their experience with previous actual Level 1 samples that individual compounds could not be identified by FT-IR. (Until recently, only FT-IR was run on samples.) They stated that the "simplicity" of the samples affects the IR interpretation by making it easier to match reference spectra than it would be in real samples. How they feel the sample "simplicity" relates to LRMS was not indicated. Also, they noted that they rarely observe fused ring aromatic hydrocarbons in fraction 4. Generally they find them in fraction 2 or 3. They also stated that there was not a very wide variety of compound types because four of the six samples had fused ring aromatics. They felt that this affected the test results because of their belief that LRMS is better than IR for fused ring aromatics whereas the contrary is true for highly polar compounds. Thus, they indicated that this was a better test for LRMS than for IR. Contractor B added that each laboratory gets more value from data obtained on their own instruments, LRMS included.

The arguments for and against simple synthetic mixtures have already been presented in a previous section. However, "B's" argument is that the spectra were actually too easy rather than lacking in significant inputs ("A's" argument).

One final note--"B" stated that although the LRMS analyst had 10 years of MS interpretation experience, he had done no previous Level 1 interpretation.

6.1.3.3 Contractor C Test Spectra Results and Comments--

Contractor C correctly identified 11½ out of 13 categories and 25 out of 30 compounds in the test spectra. All categories were correctly identified in all spectra except LC6b. All compounds in LC4a, LC4b, and LC6a were correctly identified. Most of the incorrect compound assignments were in LC5b and LC6b. The 5 compounds missed by "C" were also missed by the other three contractors. Contractor C was the only contractor to correctly identify 2,3-benzofluorene in LC5a, phenazine in LC5b, and o-phenoxybenzoic acid in LC6b.

In both LC4a and LC4b the Level 1 LRMS report was correctly completed with the category assignment fused alternate, nonalternate hydrocarbons,

MW <216. In the interpretation of spectrum LC4a, the assignment rationale for each compound identified was that the eight most abundant peaks for that compound were present. Anthracenes could not be distinguished from phenanthrenes by LRMS alone, as expected. The only compound(s) listed that were not included in the mixture were pyrene/fluoranthene (m/e 202) and, indeed, the eight most abundant peaks for these compounds are present. Contractor D also listed pyrene at intensity 10 and thus it could be present as an impurity in LC4a. In the interpretation of spectrum LC4a, the same rationale was used and the results were the same except ethyl anthracene/phenanthrene was listed as a possibility. The intensity for naphthalene was listed as 10 although it was the major component of LC4b. In both cases (LC4a and LC5b), the eight most abundant peaks were listed for each compound reported on the forms provided.

The Level 1 LRMS report form was correctly completed for LC5a with regard to compounds and categories with heterocyclic nitrogen compounds and fused alternate, nonalternate hydrocarbons MW <216 listed. In the interpretation of spectrum LC5a, the assignment rationale for all compounds reported was once again the presence of the eight most abundant peaks except for ethyl carbazole where, in addition, the relative abundances for the eight peaks were used to distinguish ethyl carbazole from dimethyl carbazole. Methyl pyrene and benzofluorene were indistinguishable in the spectrum due to nearly identical reference spectra peaks. Fluorene was not reported perhaps because many of the fluorene ions were common to the carbazoles in the spectrum. Methyl carbazole (m/e 181) was reported although not included in the spectrum. Methyl carbazole may be present as an impurity since Contractors A and D also reported it and since the molecular and fragment ions cannot be attributed to the expected compounds.

The Level 1 report form for LC5b was correctly completed with heterocyclic nitrogen compounds reported as the major category (intensity 100) and ketones the minor category (intensity 10). In the interpretation of spectrum LC5b the assignment rationale for most compounds identified was the presence of the eight most abundant peaks. The isomers 7,8-benzoquinoline and phenanthradine were both listed as possibilities while anthrone and 1,10-phenanthroline were not listed. Instead, methyl benzo(h)quinoline and methyl benzo(c)-cinnoline were listed as present with their assigned molecular ions corresponding to anthrone's molecular ion and M-1 fragment. Finally, dimethyl

benzoquinoline and anthraquinone/dimethyl benzo(c)cinnoline were listed at m/e 207,208. These may be present as impurities but the interpretation suggests that the assignments for these ions were based, in part, on finding the methyl homologs reported instead of anthrone.

The Level 1 report form was correctly completed for LC6a with the category assignments amides (intensity 100) and phenols (intensity 10). In the interpretation of LC6a, the assignment rationale was that a good match was achieved with a reference spectrum of the compound listed. In most cases this included the eight most abundant peaks. Pyridone was listed instead of hydroxypyridine and was considered acceptable due to the tautomerization of the compound. Fraction 6 being the proper fraction for phenols to elute in was also used as justification for finding o-6-biphenol in LC6b.

Although ketones and carboxylic acids were correctly identified in LC6b, phenols were missed. In the interpretation of LC6b the assignment rationale included inputs other than just the eight most abundant peaks because no reference spectrum or eight peak list for fluorene carboxylic acid could be found. The loss of the acid group (COOH , -45 m/e) from the molecular ion (m/e 210) yielded the 165 peak which, upon rearrangement of the proton, gave the peak at 166 indicative of the fluorene ring. Thus, on the basis of this argument and because "C" noted that this was the proper LC fraction for carboxylic acids, fluorene carboxylic acid was identified. Contractor B also made essentially the same argument for finding this compound. The other two compounds correctly identified, o-phenoxybenzoic acid and 9-fluorenone-4-carboxylic acid, were identified based on the seven most abundant peaks listed for each compound. Dimethyl phenol was probably not identified because the molecular ion is also a fragment ion for o-phenoxybenzoic acid. Fluorenone was also not identified although the molecular ion was rather intense and the fragment ions were also present. However, the relative intensities for the molecular ion and fragments were not the same as predicted for the pure compound. The category assignment carboxylic acids was correct for the three compounds identified although o-phenoxybenzoic acid could also be classified as an ether and 9-fluorenone-4-carboxylic acid as a ketone. Fluorenone carboxylic acid was listed as the major component, although it is present in amounts nearly equal to the other LC6b components. It was given a 100 intensity rating probably because the molecular ion 224 was the most intense ion in the spectrum.

Although the contractor made no additional comments and gave no additional clues as to the means by which the spectra were interpreted, it is clear that (1) reference lists of eight most abundant peaks were consulted, and (2) molecular ions were probably searched for initially.

6.1.3.4 Contractor D Test Spectra Results and Comments--

Contractor D correctly identified 6½ out of 13 categories in the test spectra, and 17 out of 30 compounds. All categories were correctly identified in all spectra except LC5a, LC6a, and LC6b. All compounds in LC4a and LC4b were correctly identified. Most of the incorrect category and compound assignments were in LC6a and LC6b. Of the 13 compounds missed by "D", 5 were missed by three other contractors and 3 were missed by two other contractors.

The signal assignments and LRMS report forms for LC4a and LC4b indicated that all of the mixture categories, compounds, or their isomers were found at the proper intensities. In the interpretation of LC4a and LC4b, the assignment rationale was that the very strong, even mass, high mass peaks suggested the presence of polynuclear aromatic materials even though these materials are not typically found in fraction 4. The lack of mass intensity at low mass suggested that few if any heteroatom species other than fused ring compounds are present. All the molecular ions and several fragment ions used to make the interpretations were grouped separately making it impossible to say which fragment belonged to a given molecular ion. Acenaphthene (m/e 152) and pyrene (m/e 202) were listed as possible minor components in LC4a (and traces of a nitrogen containing heterocycle [m/e 209]). Contractor C also reported pyrene in LC4a so it may be present as an impurity. In LC4b the analyst correctly noted that anthracene was one of the major components and the alkylated anthracenes were not. However, a C4 branched naphthalene not in the mixture was listed as a minor (intensity 1) component in LC4b, along with acenaphthene (intensity 10). Also, acridine (m/e 179) was listed as a major component although it is not in the spectrum. Apparently the 179 peak assigned as the molecular ion for acridine is actually the M + 1 isotope peak of anthracene/phenanthrene even though six out of eight acridine peaks are present. This indicates that just because the reference peaks are present the compound may not be. Other inputs must also play a part in the interpretation. In the LRMS report for LC4b, heterocyclic

nitrogen, the category in which "acridine" (intensity 100) falls, was given a 10 intensity ranking. This is not consistent. In both LC4a and LC4b the anthracenes and naphthalenes, etc., were given the category listing fused ring aromatics MW 178-206.

In LC5a the assignment rationale was that the spectrum consisted of a group of N-heterocycles showing fragmentation from rather strong molecular ions. As long as the molecular ions were present, spectral interpretation was easy and positive judgments could be made. It was stated that fused ring aromatics normally give such peaks. Again, a list of the molecular ions and fragment ions was given. The signal assignments were for a series of alkylated carbazoles and indoles. The molecular ion for fluorene was not listed and the molecular ion for benzofluorene (m/e 216) was listed as unsigned. Fluorene was deleted because the analyst assumed m/e 166 belonged only to carbazole. The four correctly assigned compounds were listed at the proper intensities on the LRMS report form. In addition, methyl carbazole and propyl carbazole were listed as minor components apparently based on finding ethyl carbazole and assuming that a homologous series of alkylated carbazoles was present. However, it is possible that these compounds were present as impurities.

Both categories present in LC5b were correctly reported although the identification of ketones was based on an incorrect assignment and thus the intensity given was 100 instead of 10. The rationale for the interpretation of spectrum LC5b was based in part on the IR interpretation (in this case the two could not be separated) and on the results of LC4b. The contractor stated that finding the two peaks at adjacent mass (179, 180) with no knowledge if they rise and fall together over a heating cycle made the interpretation difficult. More information (other spectra) were stated as necessary for a positive identification along with chemical ionization (CI) data on this fraction. In this particular case, the contractor attempted to correlate LC5b with LC4b by assuming these spectra were taken from the LC fractionation of a single sample when, in fact, each was from a separate unique mixture. Acridone (179) was identified and, as an isomer of the two mixture components 7,8-benzoquinoline and phenanthradine, was considered correct. Fluorenone (180) was listed instead of phenanthroline and phenazine. Methyl acridine and methyl fluorenone were listed as minor components, part of an alkylated

homologous series, although these peaks were probably mistaken for anthrone. Chalcone (208) was listed as a trace component (intensity 1).

The LRMS report category assignment for LC6a was for ether, which was not present. In LC6a the rationale was that little information could be gained due to the absence of recognizable molecular ions (because the compounds in the fraction obviously fragmented significantly). The low mass peaks observed, however, can be assigned to several functional groups. The contractor stated that IR data or CI-LRMS data are required for assignment. The peaks at 180, 95, and 65 were judged to be consistent with phenyl ether but the assignment was not based on solid evidence. Two of the ions listed, though, corresponded to two of the three molecular ions in the spectrum.

The category assignment for xanthenes (i.e., ketones) was correct for several of the actual components of LC6b. The LC6b assignment rationale was that the high mass ions in this spectrum were unusual for LC6. The materials the contractor normally finds in this fraction fragment to give a significant ion abundance at low mass. The series, starting with m/e 196, 210 (C_1), and 224 (C_2), is consistent with a series of alkylated xanthenes, but the peak intensities are the reverse of that expected. A list of typical species from a type of source (coal burning, exhaust, etc.) would be helpful in these interpretations. The source type for this work is not given and would help in the interpretation. Also m/e 179 and 180 were listed as possible carryovers from LC5b, again indicating that the contractor assumed that the spectra were all from a single sample.

The following general conclusions were drawn from "D's" interpretation of the test spectra:

1. Interpretation was aided and sometimes based solely on the presence of easily recognizable molecular ions.
2. Assignment rationales for certain spectra suggested that the contractor was unfamiliar with the type of compounds in the spectra.
3. LC fraction data are a significant input to the interpretation.

The contractor made a number of comments regarding the quality of the LRMS and IR spectra and additional inputs they felt were important to the interpretation. "D" commented:

Only a small part of the mental process of interpretation can be effectively reduced to paper. Experience and intuition play a

very important role. The person interpreting a spectrum does not always know which characteristics trigger a response. A general visual survey of a spectrum often causes recall of a similar spectrum and initiates the process of ultimate compound identification.

Interpretation of LRMS data is basically instinctive. The use of reference spectra, correlation tables, and experience are the main elements in the identification of compound types. A study of the high mass peaks gives an indication of compound stability which can be used as an aid in interpretation. More LRMS spectra taken during a heating cycle would help associate peaks originating from a single compound. Also analog records provide a greater dynamic range and if a single focusing magnetic instrument is used, metastable ions aid in association of peaks. Low ionization voltage (7-10 eV) or CI (methane or isobutane) are useful techniques for identifying molecular ions in a complex mixture. Given the molecular weight, spectral interpretation is much easier.

In a general sense the knowledge of source type is also important. The types of compounds emitted from an incinerator are different than a coal burning power plant. The spectra presented for interpretation were exceptionally clean. Normal Level 1 samples are more complex and carryover from one fraction to another is common.

6.2 LRMS ANALYSIS OF TEST SAMPLES

6.2.1 Overview of All Results

Based on the results reported by the contractors for the test spectra, two synthetic mixtures and a coal gasification tar sample were prepared and sent to the four contractors for analysis on their instruments and by interpretation as before. The test samples prepared were designated LC5 and LC6 and contained mostly compounds and categories identified incorrectly by at least three out of four contractors in the test spectra and thus were inherently more challenging for these contractors than were the test spectra. Category and compound assignments of these two mixtures are shown in Tables 39 and 40. Sample LC5 contained mostly heterocyclic nitrogen compounds with minor (<10 percent) amounts of ketones and fused alternate hydrocarbons. Mixture LC6 contained nearly equal amounts of ketones and acids with a small quantity of phenols. As stated above, many of the compounds in these mixtures were in the test spectra mixtures. Sample LC5 had fluorene and benzofluorene present as fused alternate hydrocarbons; 7,8-benzoquinoline, 1,10-phenanthroline, phenazine, and 2,6-dimethyl quinoline as heterocyclic nitrogen compounds; and anthrone as a ketone. Only 2,6-dimethyl quinoline was new to

TABLE 39. CATEGORIES CORRECTLY IDENTIFIED BY CONTRACTORS IN LC5 AND LC6
TEST SAMPLES BY LRMS

Category	mg/L	Weight %	Contractor			
			A	B	C	D
LC5	Fused alternate nate hydrocarbons	1,748	10	NR*	20	20
	Heterocyclic nitrogen compounds	17,042	110	160	430	120
	Ketone	1,522	111	100	20	111
	Ketone†	7,027	200	100	30	10
LC6	Acid†	8,975	NR	40	110	NR
	Phenol	1,078	NR	NR	10	10
Total correct out of 6			4	4	6	5

NR = Not reported.

*Although a compound belonging to this category was identified, the category itself was not listed.

†9-Fluorenone-4-carboxylic acid was placed in acid category.

TABLE 40. COMPOUNDS CORRECTLY IDENTIFIED BY CONTRACTORS IN LC5 AND LC6
TEST SAMPLES BY LRMS

	Compound	MW	mg/L	Weight %	Contractor			
					A	B	C	D
LC5	Fluorene	166	908	4.5	NR	NR	10	10
	2,3-Benzofluorene	216	840	4.1	NR	NR	10	10
	7,8-Benzoquinoline	179	3,936	19.4	100*	100*	100	100*
	1,10-Phenanthroline	180	6,294	31.0	NR	NR	10	NR
	Phenazine	180	3,405	16.8	NR	NR	100	NR
	2,6-Dimethyl quinoline	157	3,407	16.8	NR	30	100	10
	Anthrone	194	1,522	7.5	10	NR	NR	NR
	9-Fluorenone	180	4,461	26.1	100	100	10	10
LC6	1-Fluorene carboxylic acid	210	1,888	11.1	NR	NR	10	NR
	9-Fluorenone-4-carboxylic acid	224	7,087	41.5	NR	40	100	NR
	2-Methyl-1-tetralone	160	892	5.2	NR	NR	10	NR
	2-t-Butyl phenol	150	1,078	6.3	NR	NR	10	10
	2-Methyl-1,4-naphthoquinone	172	1,674	9.8	NR	NR	10	NR
Total correct out of 13					3	4	12	6

NR = Not reported.

*Phenanthradine and acridine are isomers of 7,8-benzoquinoline and were considered correct identifications here.

this mixture. Sample LC6 contained 9-fluorenone, methyl tetralone and methyl naphthoquinone as ketones, fluorene carboxylic acid and fluorenone carboxylic acid as acids, and butyl phenol as the phenol. Fluorenone and fluorenone carboxylic acid were the major components of LC6 with the other compounds present at less than 10 percent of the mixture. Butyl phenol, methyl naphthoquinone, and methyl tetralone were new to this mixture. Acids and phenols were again problem categories for "A" and "D". Other categories were, in general, correctly identified in both samples, although again the intensities assigned were usually wrong. Overall, "C" correctly identified all 6 categories as well as 12 out of the 13 compounds in LC5 and LC6. The other contractors were not as successful, missing at least one or two categories, usually in LC6, and identifying only three to five compounds. Each of the compounds missed by all contractors in the test spectra was identified by at least one of the contractors in the test samples, indicating that the contractors did gain more information when they could analyze the samples themselves. Phenazine, 1,10-phenanthroline, and anthrone in LC5 were missed by three out of four contractors while fluorene COOH, methyl tetralone, and methyl naphthoquinone were missed by three out of four in LC6. The intensity assignments, in general, did not correctly reflect the actual composition of the sample.

Differences in the interpretations were revealed by constructing tables comparing molecular ion assignments (Table 41), all ions reported for a given expected compound (Table 42), and a listing of compounds reported that were not included in the sample (Table 43). This same approach was used to evaluate the test spectra results. Once again the types of errors suggested by the test spectra results were apparent. Contractor B missed 7 out of the 13 compounds and "D" missed 4 because the molecular ions for these compounds were never identified. Several molecular ions were again reported as fragment ions for other compounds not in the mixture. As shown in Table 44, almost half of the errors made by the contractors were a result of their not finding the molecular ions for the mixture compounds with most of these cases occurring in LC6. The remaining errors were mostly a result of assigning the wrong compound name to a molecular ion or assigning the molecular ion as a fragment of another compound. Contractors A, B, and D all incorrectly assigned molecular ion 180 in LC5 to fluorenone rather than to the correct assignments phenazine and 1,10-phenanthroline, probably because 180 is an

TABLE 41. CONTRACTORS LRMS SIGNAL ASSIGNMENTS FOR SPECIFIC MOLECULAR IONS IN THE LOW RESOLUTION MASS SPECTRA THEY GENERATED FROM THE TEST MIXTURES

Fraction	Ion	Expected	Contractor			
			A	B	C	D
LC5	166	Fluorene	NA	NA	Fluorene, fragment of methyl phenanthroline or methyl benzo[c]cinoline	Fluorene
	216	2,3-Benzofluorene	Methyl pyrene	NA	2,3-Benzofluorene or methyl pyrene	Benzofluorene
	179	7,8-Benzoquinoline	Acridine, phenanthridine, etc.	Acridine	Benzo[h]quinoline, acridine; phenazine and 1,10-phenanthroline fragment	Acridine
	180	1,1-Phenanthroline, phenazine	Fluorene	Fluorenone or methyl-fluorene	Phenazine, 1,10-phenanthroline, anthraquinone fragment	Fluorenone
	157	2,6-Dimethyl quinoline	NA	Dimethyl quinoline	Dimethyl quinoline	Dimethyl or ethyl quinoline
	194	Anthrone	Anthrone	NA	Methyl phenanthroline or methyl benzo[c]cinnoline; fragment of methyl benzoquinoline or beta-naphthaquinoline	Methyl fluorenone
	180	9-Fluorenone	Fluorenone	Fluorenone	Fluorenone or 1-phenalenone	Fluorenone
	210	1-Fluorene carboxylic acid	Unknown	NA	Fluorene carboxylic acid	NA
LC6	224	9-Fluorenone-4-carboxylic acid	Hydroxy anthraquinone	Carboxy fluorenone	9-Fluorenone-4-carboxylic acid	NA
	160	2-Methyl-1-tetralone	NA	NA	Methyl tetralone	NA
	150	2-t-Butyl phenol	Fluorenone fragment	NA	t-Butyl phenol; fragment of fluorenone or 1-phenalenone; fragment of 9-fluorenone-4-carboxylic acid	t-Butyl phenol
	172	2-Methyl-1,4-naphthoquinone	Ethoxy naphthalene	NA	Methyl naphthoquinone	NA

NA = Not assigned.

TABLE 42. LRMS SIGNAL ASSIGNMENTS FOR COMPOUNDS IN THE SPECTRAL INTERPRETATION TEST MIXTURES

	Compound	MW	Weight %	Contractor			
				A	B	C	D
LC5	Fluorene	166	4.5	NR	NR	166,165,82.5,167 163,83,164,82	166
	2,3-Benzofluorene	216	4.1	NR	NR	216,215,217,94.5, 108,107.5,213, 106.5	216
	7,8-Benzoquinoline	179	19.4	179,151,89	NR	179,178,89.5,151, 76,89,152	179
	1,10-Phenanthroline	180	31.0	NR	NR	180,179,154,153, 128,90,76,63	NR
	Phenazine	180	16.8	NR	NR	180,179,154,153, 128,90,76,63	NR
LC6	2,6-Dimethyl quinoline	157	16.8	NR	157	157,115,142,39, 51,63	157
	Anthrone	194	7.5	193,194	NR	NR	NR
	9-Fluorenone	180	26.1	180,152,151,150, 76,75	180	180,152,151,150, 126,76,63,51,50	180
	1-Fluorene carboxylic acid	210	11.1	NR	NR	210,166,165	NR
	9-Fluorenone-4-carboxylic acid	224	41.5	NR	224	224,207,196,179, 168,151,150,139	NR
	2-Methyl-1-tetralone	160	5.2	NR	NR	160,145,131,118, 90,39	NR
	2-t-Butyl phenol	150	6.3	NR	NR	150,135,107,91, 77,39	150
	2-Methyl-1,4-naphthoquinone	172	9.8	NR	NR	172,144,116,115, 104	NR

NR = Not reported.

TABLE 43. COMPOUNDS REPORTED THAT WERE NOT INCLUDED IN THE TEST MIXTURES

Contractor	Compound	LC fraction	LRMS Intensity	MW	Mistaken for
A	Acridine	5	100	179	7,8-Benzoquinoline
	Fluorenone	5	100	180	1,10-Phenanthroline and phenazine
	Methyl carbazole	5	10	181	Unknown
	Methyl pyrene	5	10	216	2,3-Benzofluorene
	Anthraquinone	5	1	208	Unknown
	Hydroxyanthraquinone	6	100	224	9-Fluorenone-4-carboxylic acid
B	Ethoxy naphthalene	6	10	172	2-Methyl-1,4-naphthoquinone
	Unidentified	6	10	210	1-Fluorene carboxylic acid
	Acridine	5	30	179	7,8-Benzoquinoline
	Fluorenone or methylfluorene	5	100	180	Phenazine or 1,10-Phenanthroline
C	Methyl acridine	5	30	193	Anthrone fragment
	Anthraquinone	5	10	208	Unknown
	9,9'-Dianthraquinone	5	10	384	Unknown
	Acridine	5	100	179	7,8-Benzoquinoline
	Methylbenzoquinoline or beta-naphthoquinoline	5	10	193	Anthrone fragment
	Methyl phenanthroline or methylbenzo(c)cinoline	5	10	194	Anthrone
	1-Phenalenone	6	10	180	9-Fluorenone
	Acridine	5	100	179	7,8-Benzoquinoline
D	Methyl acridine	5	10	193	Anthrone fragment
	Fluorenone	5	100	180	1,10-Phenanthroline, phenazine
	Methyl fluorenone	5	10	194	Anthrone
	Anthraquinone	5	1	208	Unknown
	Methyl phenyl indole	6	10	207	Fragment of 9-fluorenone
	Unknown homologous series	6	100, 100, 100	196, 224, 210	4-carboxylic acid
					9-fluorenone-4-carboxylic acid molecular ion and fragment, molecular ion for 1-fluorene-carboxylic acid

TABLE 44. ERRORS MADE BY CONTRACTORS IN INTERPRETING
LOW RESOLUTION MASS SPECTRA THEY GENERATED FROM
TEST SAMPLES LC5 AND LC6

		Contractor				Total
	Test mixture	A	B	C	D	
1. Did not find molecular ion at all.	LC5	2	3	0	0	3
	LC6	2	4	0	4	9
2. Found molecular ion but left unidentified.	LC5	0	0	0	0	0
	LC6	1	0	0	0	1
3. Found molecular ion but identified compound incorrectly (either as fragment or as another compound).	LC5	3	2	1	3	8
	LC6	2	0	0	0	2
		10	9	1	7	23

even molecular weight and because the analysts are used to seeing only odd-numbered molecular ions for N compounds. The same patterns of interpretation were again present, with "A" and "C", in general, reporting several peaks for each compound identified and "D" and "B" reporting only molecular ions. Once again, "D" listed some fragments but listed them separately and not with the corresponding molecular ions.

6.2.2 Results and Comments from Specific Contractors

6.2.2.1 Contractor A Test Mixtures Results--

Contractor A correctly identified 4 out of 6 categories and 3 out of 13 compounds in the test mixtures. All three categories in LC5 were identified correctly but both acids and phenols were missed in LC6. Only benzoquinoline (identified as acridine) and anthrone in LC5 and fluorenone in LC6 were identified by LRMS alone. The same type of signal assignments and assignment rationales were given by "A" for their analyses of LC5 and LC6 with the main difference between these interpretations and those for the test spectra being the use of spectra taken at varying probe temperatures and ionizing voltages (15 eV and 70 eV).

In LC5, the assignment rationale was that species for this fraction were generally assigned on the basis of reference spectra, vaporization behavior, and 15-70 eV spectral characteristics. The three categories present were identified correctly in the LRMS report form but ketone was assigned an intensity of 100 instead of the expected 10 because peak 180 (1,10-phenanthroline and phenazine) was incorrectly assigned as a ketone (fluorenone). Methyl pyrene was assigned to MW 216 instead of benzofluorene. The reason given for the assignment was that although "methyl pyrene" is displaced two LC fractions from its normal location, it does show a match with a reference spectra for six of the eight most abundant peaks, which is accurate both in relative intensity and in covaporization. This explanation is significant in that in test spectra LC5a, 2,3-benzofluorene (216) was listed as possibly being methyl pyrene but this was discounted as being possible because of the lateness of the LC fraction. In test mixture LC5 though, as a result of confirming evidence from the probe heating cycle, 216 was listed as belonging to a fused alternate-nonalternate hydrocarbon. The molecular ions for fluorene (166) and dimethyl quinoline (157) were not reported. Methyl carbazole was assigned to peak 181 (actually belongs to

phenanthroline) because the peak was too large to be an isotope of 180. This is probably because 180 is saturated in the scans in which both it and 181 are prominent, and because 180 is the combined sum of the intensity for 1,10-phenanthroline and phenazine. Anthraquinone (208) was listed as present. Contractors C and D also assigned 208 to anthraquinone (intensity 1). Anthraquinone could be present as an impurity in the mixture. The probe spectra "A" obtained on LC5 and gave in their report show spectra taken over the heating range 80° to 270° C, mostly at 70 eV with several at 15 eV. The objective of the presentation of the spectra was to show how certain peaks appear and disappear together during the heating cycle and thus establish a link among them as possibly belonging to the same compound. Spectra taken at 15 eV were so taken under the assumption that predominantly molecular ions would be present. Of the two molecular ions not reported by "A" in LC5, fluorene (166) and dimethyl quinoline (157) both are listed in several of the 70 eV spectra and both are present in one of the 15 eV spectra although at very low intensities (<1 percent). The computerized printout of the data sometimes did not agree with the peaks listed. For example, in the probe scan at 70 eV, 75° C, peaks at what the m/e scale indicates to be 165 are identified by the computer as 166.

In the interpretation of LC6, three molecular ions were identified and compounds were assigned to each using somewhat different rationales. Fluorenone was correctly assigned to peak 180 because fluorenone had a good reference spectrum match and was consistent with the LC fraction and IR information. Ion 224 was incorrectly assigned to hydroxyanthraquinone. The assignment rationale was that hydroxyanthraquinone was the best match available although less than perfect. The m/e 207, 206 pair may, depending on the isomer, come from this compound since they appear to covaporize. Molecular ion 172 was incorrectly assigned to ethoxy naphthalene on the basis of it being the best available match for the m/e 172, 144, and 115 peaks, which were found to covaporize. Fluorenone and hydroxyanthraquinone were both listed as major components (intensity 100) on the LRMS report form and ethoxy naphthalene was listed as a minor component (10 intensity). Another species listed as unclassified was thought to be due to peaks at 165 and 210 with 165 the major fragment ion of the molecular ion (210) of fluorene carboxylic acid. So, although only one of the LC6 mixture compounds was correctly identified, four of the six molecular ions were identified. Probe

data for LC6 consisted of spectra taken over the heating cycle from 80° to 230° C with several spectra taken at 15 eV. The molecular ions and major fragments for methyl tetralone (160) and butyl phenol (150) were not present in the probe spectra for these mixtures. It is possible that because both are volatile liquids, they were lost due to evaporation prior to the probe analysis. It is reasonable to expect this and probable that the ions for these compounds would be visible in batch inlet spectra. However, batch spectra were not taken for LC6. Butyl phenol volatilizes at 237° C and the probe data given stopped at 230° C. However, "C" found butyl phenol and stopped at 120° C. The general conclusions drawn from "A's" analysis and interpretation of LC5 and LC6 are that temperature and eV variations are useful means to identify molecular ions and link them to fragment ions. Volatile organics like methyl tetralone will be lost prior to the probe run via coevaporation with the solvent. The analyst also found that only a part of each entire probe run provided useful information. Also, it is likely that the appearance of certain ions in early spectra affected the choice of ionizing voltages used later. Thus, certain decisions about the interpretation were made during the analysis of the mixtures.

6.2.2.2 Contractor B Test Mixture Results--

Contractor B correctly identified 4 out of 6 categories and 4 out of 13 compounds in LC5 and LC6. The fused alternate nonalternate hydrocarbons in LC5 were not identified (fluorene, benzofluorene) nor was the phenol (butyl phenol in LC6). Benzoquinoline (identified as acridine) and dimethyl quinoline were identified in LC5 and fluorenone and fluorenone COOH were identified in LC6. All spectra were probe spectra run at 70 eV.

It is difficult to determine "B's" assignment rationale for compounds identified in mixture LC5 and LC6 because the designated forms were not completed as requested. However, "B" did provide copies of the spectra (summation of all scans) obtained on LC5 and LC6. The analyst also marked several of the peaks that were apparently used in making the interpretation. In LC5, acridone (7,8-benzoquinoline) was probably identified on the basis of the strong ion at m/e 179 and was assigned an intensity of 100. Dimethyl quinoline was also identified on the basis of the molecular ion at 157. In addition, three fragment ions for dimethyl quinoline were marked on the spectra. Dimethyl quinoline was assigned an intensity of 30, apparently

based on the relative intensity of the molecular ion 157. Fluorenone or methyl fluorenone was incorrectly assigned to m/e 180, which should have been assigned to phenanthroline and phenazine. Methyl acridine was incorrectly assigned to 193 (homolog error). Ion 193 probably belongs to anthrone. Interestingly, all molecular ions and major fragments for the compounds in LC5 were present at significant intensities in the spectra "B" generated.

The interpretation of LC6 was again based largely on finding and identifying molecular ions. Fluorenone and carboxyfluorenone were both correctly reported. Carboxyfluorenone was listed as an aromatic ketoacid. This is also correct because both functional groups are present. Again, except for the tetralone molecular ion, all of the molecular ions and major fragments were present in the spectra generated by Contractor B for LC6.

Two observations can be made from these data. Contractor B's spectra are of sufficient quality to facilitate interpretation and identification of all of the mixture compounds. The spectral data, however, were not fully utilized. Finally, although the report stated that both LRMS and IR analysts worked together on the interpretation, it was in some cases possible to separate the two interpretations.

6.2.2.3 Contractor C Test Mixture Results--

In mixtures LC5 and LC6, "C" identified all 6 categories correctly and 12 out of 13 compounds. Both mixtures were analyzed by both probe (direct evaporation) and batch (reference) inlets at 70 eV. The contractor stated that all compounds identified were seen in both batch (120° C) and probe spectra (20°-300° C). For all compounds listed for LC5 and LC6, the assignment rationale was that the most abundant peaks for the compounds were present. The molecular ion (194) for the compound missed in LC5, anthrone, was instead listed for methyl phenanthroline (homolog error) or methyl benzo(c)cinoline. One of the anthrone fragments (193) was also listed for methyl benzoquinoline (homolog error) or beta-naphthoquinaldine. Although anthrone, the only ketone in LC5, was missed, the category ketones was listed based on the assignment of anthraquinone (208) and 9,9'-dianthraquinone (384), which were not included in the mixture but could be present as impurities because three out of four contractors reported anthraquinone. All of the compounds that were correctly identified were also listed at the proper intensities (based on their weight percent contribution to the mixtures).

In mixture LC6 all compounds were identified correctly and no additional compounds were reported. The assignment rationale was, in general, the same as for LC5. Proper LC fraction for ketones, acids, or phenols was also used to justify the presence of many of the assigned compounds. Methyl naphthoquinone's assignment rationale was based on published mass spectra of other substituted naphthoquinones in which the molecular ion is usually the base peak. The published mass spectrum (Eight Peak Index) for 2-methyl naphthoquinone has no molecular ion (172 is listed at 0.00 intensity), and is inconsistent with the spectra of naphthoquinone. The rationale for assigning fluorene carboxylic acid was that, although no reference spectrum could be found, loss of the acid group from the molecular ion yielded the 165 peak and, with rearrangement of the H, gave the peak at 166 representing the fluorene ring.

Contractor C's batch and probe spectra for LC5 and LC6 were obtained by oscillographic traces. The molecular ions and fragments for each compound reported were noted on each spectrum.

6.2.2.4 Contractor D Test Mixture Results--

Contractor D correctly identified 5 out of 6 categories and 6 out of 13 compounds in LC5 and LC6. Both of the acids were missed in LC6 along with methyl tetralone and methyl naphthoquinone. Phenanthroline, phenazine and anthrone were missed in LC5. Both mixtures were run on probe inlet at 70 eV.

The assignment rationale for LC5 was based in part on the IR data, which were studied concurrently with the mass spectral data. The LRMS analyst stated that there appeared to be two components with a MW of 180; one contains two nitrogens (possibly $\text{-C}\equiv\text{N}$) and the other is a ketone. The compounds that came off the probe at higher temperatures (MW = 193 and 194) appeared to be related to the materials at m/e 179 and 180 but at a lower concentration and higher temperature. A peak at 150 appeared early in the heating cycle but was not identifiable. Most compounds appeared to be identified on the basis of their molecular ions. Benzofluorene, acridine (benzoquinoline), dimethyl quinoline, and fluorene were identified correctly and listed at the proper intensities. Phenazine and phenanthroline, though not identified, both contain two nitrogens and the presence of such a compound was noted and assigned as an unknown; fluorenone was incorrectly

listed as also contributing to 180. Methyl acridine and methyl fluorenone were incorrectly listed for anthrone ions (194, 193), another case of "homolog error." Finally, a trace quantity of anthraquinone was reported. The category assignments were correct except for ketones, which were assigned 100 intensity due to the listing of fluorenone instead of anthrone.

The probe spectra for LC5 also contain some information on the interpretation process. In general, the spectra were much weaker than those reported by the other contractors. Ion 179 was noted on one of the spectra as being either acridine or benzoquinoline, although the more frequently cited acridine was listed in the report. Also methyl pyrene and benzofluorene were listed for peak 216 but "benzofluorene or isomer" was reported. An attempt was made to link 180, 154, and 127 together as part of the same compound by assuming that 154 and 127 were the fragment of 180 following the sequential loss of two $C\equiv N$ groups.

The rationale for interpretation of mixture LC6 was to assume that a homologous series of an aromatic compound was present. The major portion of the mixture could not be identified even though good spectra were produced. The absence of functional group characteristic peaks at low mass made interpretation difficult. The IR data suggested an acid, but the LRMS data could not confirm this. Therefore, it was suggested that the unidentified peaks in the low resolution mass spectra for LC6 originated from an aromatic acid. The contractor was correct in the assumption that ions 196, 210, and 224 were attributable to aromatic acids although not a homologous series. Two compounds were correctly identified--butyl phenol and fluorenone. Ion 207 was assigned to methyl phenyl indole, although no such compound was known to be present in the mixture. Ion 207 is most likely due to a fragment of 9-fluorene-4-carboxylic acid as is ion 196. The probe spectra for LC6 also indicated that ions 160 (methyl tetralone) and 172 (methyl naphthoquinone) were under suspicion as naphthalene dihydrozone and ethoxy naphthalene (also listed by "A") but these compounds were not listed on the forms. Benzocinnoline was considered a possibility for 180 along with fluorenone. Throughout the probe spectra there are indications that a homologous series was being searched for with peaks noted at intervals of -14 m/e units from suspected molecular ions. These results indicate that, in general, only high mass molecular ions were being searched for and when found, attempts were made to link them to fragments as part of a homologous series.

The contractor also had several comments on these test samples and the interpretive process employed that tend to agree with the observations noted earlier in this section:

Interpretation of LRMS data is for the most part based on one's experience with having seen similar spectra from similar sources previously. If one encounters a spectrum previously interpreted, it "triggers" something in the mind which provides in most cases an unequivocal identification. When this "trigger" is absent one must rely on characteristic fragment ions from molecular functional groups or strong molecular ions, the mass representative of molecular weight. It should be noted that virtually all the identifications made on the samples provided are of compounds which give strong molecular ions. When one has a molecular ion to work with, and if various degrees of methyl substitution are present, a positive identification of molecular weight can often be made. In many cases only one or two compounds result from such an identification when it is combined with information on sample origin. When one deals with artificial samples, however, homologous series are typically not present and interpretation is therefore more difficult.

Differences in mass spectrometer instrumentation can also cause problems in identification. LRMS data are recorded using instruments which are primarily designed for GC/MS. All of our instruments have helium flowing constantly into the ion source of the mass spectrometer resulting in spectra which are of a mixed ionization nature (some 70eV ionization and some He charge exchange ionization) and not exclusively 70eV spectra. This fact causes a mild enhancement of the molecular ion due to the lower energy of ionization which takes place. Additionally, all of our mass spectrometers are equipped to do both chemical ionization as well as electron ionization and for this reason the ion source is rather tightly closed. When large samples are introduced to these ion sources, using the direct insertion probe, a phenomenon known as "autochemical ionization" can take place. The result of this ionization process is the displacement, by one mass unit, to a higher mass for molecular ions. If this is not taken into consideration by examining spectra over a heating profile where varying concentrations of sample are passing to the ion source of the mass spectrometer, one could easily confuse a hydrocarbon compound having an even molecular weight with a nitrogen containing compound with an odd molecular weight one mass unit higher.

The two previously prepared LC fractions provided (LC5 & LC6) yielded very clean mass spectra and in the case of LC5 positive identification of several components could be made using the LRMS in conjunction with the IR data. In the case of LC6 however, the majority of the LRMS data remains unidentified. Significant intensity high mass peaks are present in the spectra which do not match any of the published spectra available in our laboratory. This is very frustrating to a mass spectrometrists who doesn't often get clean mass spectral data with which to work. Using the IR data which shows acid absorptions, it can be guessed that the unidentified peaks are aromatic acid molecular ions, but confirmation of this fact is not possible.

Interpretation of LRMS and IR data is a very personal thing and I am sure done differently by each individual given the task. To record in writing the thought process which one uses to identify compounds in a complex mixture is difficult if not impossible. It would be my suggestion that several experienced people be brought together for a discussion to further examine the process of interpreting LRMS data.

6.3 LRMS ANALYSIS OF TAR DERIVED FROM COAL GASIFICATION

6.3.1 Overview of All Results

The coal gasification tar sample described in Section 4 was to be subjected to Level 1 LC fractionation and fractions 4, 5, and 6 were to be analyzed by LRMS. The contractors were also given the option of analyzing other fractions and reporting these results if they felt such data would be useful in interpreting the results from 4, 5, and 6. Tables 45 and 46 list all categories and compounds reported by the contractors in their LC fractions 4, 5, and 6 of the tar sample. In general, the category assignments indicated the compounds were probably appearing in the proper LC fractions (± 1) with "D's" phenols in 4 and 5. Contractor A reported significantly more compounds in LC4 than did the other contractors with most of the additional compounds reported being fused alternate-nonalternate hydrocarbons that were probably carried over from fractions 2 and 3. "A" also reported more compounds in 4, 5, and 6 than did the other contractors. Contractor B, on the other hand, only reported one compound in each fraction. The disparity in reported results is also evident if the molecular weight ranges reported by the contractors are examined (Table 47). Clearly, the extent of interpretation and/or the quality of the spectra obtained must have been significantly different for each contractor to produce such diverse results. Both the quality of the spectra and the interpretation of the spectra will be examined to determine what the reasons are and if the interpretations were similar to those observed for the synthetic samples.

Tables 48 and 49 list the categories and compounds reported by at least two out of the four contractors. Heterocyclic nitrogen compounds in LC4 and phenols in LC5 and LC6 were the categories most often reported and carbazoles in LC4 and alkyl naphthenols in LC5 were the compounds most often reported. Usually each compound was reported as a member of an alkylated series.

TABLE 45. CATEGORIES REPORTED BY CONTRACTORS IN COAL
GASIFICATION FOR SAMPLE

Category	Sum of compound intensities			
	Contractor			
	A	B	C	D
LC4				
Heterocyclic nitrogen compounds	230	NR	160	300
Fused alternate, non-alternate hydrocarbons	70	NR	NR	NR
Unclassified	60	NR	NR	NR
Aliphatic hydrocarbons	NR	*	NR	NR
Phenols	NR	NR	NR	200
LC5				
Aromatic nitrile	NR	NR	100	NR
Heterocyclic sulfur	NR	NR	30	NR
Phenols	110	NR	210	220
Ketones	200	NR	NR	40
Aliphatic hydrocarbons	NR	*	NR	NR
Unclassified	10	NR	NR	20
LC6				
Phenols	340	100	310	NR
Heterocyclic nitrogen compounds	60	NR	NR	510
Ketones	10	NR	NR	NR
Unclassified	10	NR	NR	10

NR = Not reported.

*Compound was reported but intensity was not reported as required by Level 1.

TABLE 46. COMPOUNDS REPORTED BY CONTRACTORS IN COAL GASIFICATION
TAR SAMPLE USING LRMS

Compound	MW	Contractor			
		A	B	C	D
LC4					
Carbazole	167	100	NR	100	100
Benzocarbazole	217	100	NR	NR	NR
Alkylcarbazoles	181-209	10	NR	NR	NR
Alkylbenzocarbazoles	231-245	10	NR	NR	NR
Dibenzocarbazole	267	10	NR	10	NR
Dimethyl or ethyl carbazole	195	NR	NR	10	NR
Methyl carbazole	181	NR	NR	10	NR
Carbazole-C ₁ -C ₂	181-195	NR	NR	NR	100
Methyl naphthoquinoline	217	NR	NR	10	NR
Dimethylnaphthoquinoline or ethyl	231	NR	NR	10	NR
Naphthoquinoline	203	NR	NR	10	NR
Fluoranthene	202	10	NR	NR	NR
Pyrene	202	10	NR	NR	NR
Benzanthracene	228	10	NR	NR	NR
Chrysene	228	10	NR	NR	NR
Perylene	252	10	NR	NR	NR
Benzpyrenes	252	10	NR	NR	NR
Benzperylenes	276	10	NR	NR	NR
Polycyclic species	189-304	10	NR	NR	NR
Alkylated polycyclics	200-500	10	NR	NR	NR
Aliphatic hydrocarbon	43,57,91	NR	*	NR	NR
Pyridine C ₁ -C ₃	93-121	NR	NR	NR	100
Naphthol	144	NR	NR	NR	100
Alkyl naphthols	158-226	NR	NR	NR	100
Unidentified	259	10	NR	NR	NR
Unidentified	358	10	NR	NR	NR
Unidentified	390	10	NR	NR	NR
Unidentified	422	10	NR	NR	NR
Unidentified	189-304	10	NR	NR	NR
LC5					
Alkyl naphthenols	158-242	10	NR	NR	10
Naphthol	144	NR	NR	NR	10
Methyl naphthol	158	NR	NR	100	NR
Dimethyl naphthol	172	NR	NR	100	NR
Naphthol C ₁ -C ₂	158-172	NR	NR	NR	10
Trimethyl naphthol	186	NR	NR	10	NR
Alkyl biphenyl-ols	170-240	100	NR	NR	NR
Phenyl phenols C ₁ -C ₄	170-226	NR	NR	NR	10
Alkyl fluorenones	180-250	100	NR	NR	NR
Alkyl dibenzofurans	168-252	100	NR	NR	NR
Phenol	94	NR	NR	NR	100

(continued)

TABLE 46. (continued)

Compound	MW	Contractor			
		A	B	C	D
LC5 (continued)					
Phenols C ₁ -C ₃	108-136	NR	NR	NR	100
Benzophenone	182	NR	NR	NR	10
Benzophenone C ₁ -C ₅	196-252	NR	NR	NR	10
Phthalo, isophthalo or terephthalonitrile	128	NR	NR	100	NR
Anthraquinone	208	NR	NR	NR	10
Methyl anthraquinone	222	NR	NR	NR	10
Aliphatic hydrocarbon	43,57,91	NR	*	NR	NR
Methyl, dimethyl dibenzo-thiophene	198,212	NR	NR	10	NR
Unidentified	100-275	10	NR	NR	10
Unidentified	165,179	NR	NR	NR	10
LC6					
Quinoline	129	10	NR	NR	100
Alkyl quinolines	143-157	10	NR	NR	NR
Acridine	179	10	NR	NR	100
Alkyl acridines	193-207	10	NR	NR	NR
Methyl acridine	193	NR	NR	NR	10
Quinoline C ₁ -C ₃	157-185	NR	NR	NR	100
Trimethyl or isopropyl phenol	136	NR	NR	10	NR
Dimethylphenol	122	NR	NR	100	NR
3-Ethylphenol	122	NR	100	NR	NR
Phenol	94	100	NR	100	NR
Cresol	108	100	NR	100	NR
Methylcresol	122	100	NR	NR	NR
Alkylphenols	136-178	10	NR	NR	NR
Naphthol	144	10	NR	NR	NR
Alkyl naphthols	158-172	10	NR	NR	NR
Alkylated Biphenyl-ols	170-254	10	NR	NR	NR
Alkyl fluorenones	180-250	10	NR	NR	NR
4-ring heterocyclic nitrogen	203	10	NR	NR	NR
5-ring heterocyclic nitrogen	229	10	NR	NR	NR
4-ring heterocyclic nitrogen	253	10	NR	NR	NR
Polycyclic material	150-300	10	NR	NR	NR
Pyridine	79	NR	NR	NR	100
Pyridines C ₁ -C ₄	93-135	NR	NR	NR	100
Unclassified	203-217	NR	NR	NR	10

*Compound reported but no intensity value given.

NR = Not reported

TABLE 47. MOLECULAR WEIGHT RANGES REPORTED BY
CONTRACTORS FOR COAL GASIFICATION TAR SAMPLE

	Contractor			
	A	B	C	D
LC4	167-500	43-91	167-231	167-195
LC5	100-252	43-91	128-212	108-252
LC6	94-300	122	94-136	79-217

TABLE 48. CATEGORIES REPORTED BY AT LEAST TWO CONTRACTORS IN
COAL GASIFICATION TAR SAMPLE

	Categories	Contractors reporting
LC4	Heterocyclic nitrogen compounds	3
LC5	Phenols	3
LC6	Phenols	3
	Heterocyclic nitrogen compounds	2

TABLE 49. COMPOUNDS REPORTED BY AT LEAST TWO CONTRACTORS IN
COAL GASIFICATION TAR SAMPLE

	Compounds	Contractors reporting
LC4	Carbazole	3
	Alkylcarbazoles	2
	Dibenzocarbazole	2
LC5	Alkyl naphthenols	3
LC6	Methyl cresol/ethyl phenol	2
	Quinoline	2
	Acridine	2
	Alkyl acridines	2
	Phenol	2
	Cresol	2

A number of the compounds reported by RTI when the tar sample was analyzed by capillary column gas chromatography/mass spectrometry were also reported by the contractors (Table 50). The GC data tend to confirm the presence of carbazole and several phenols.

To determine if the interpretation or the quality of the spectra was responsible for some of the differences observed, Table 51 was constructed. Several compounds thought to be present in the tar sample were listed as well as several others that were reported as major components by the contractors. The contractors' spectra were also searched to see if the ions for these compounds were present and, if so, if they were utilized.

In general, signal assignments were made based on molecular ions only with supportive evidence given by the finding of other members of an alkylated homologous series. Molecular ions for these compounds were present in the spectra of all contractors except for naphthol ("D") and methyl naphthol ("B"). At least in one case ("C"), several compounds (acridine, quinoline, pyridine) were not reported even though the spectra clearly showed the molecular ions and they were marked by the analyst. The contractors more often reported series of compounds rather than individual ones (for example, alkyl naphthols) although the parent compound was usually identified in these cases. For this reason it is difficult to determine solely on the basis of the tabulated data which identifications are justified and which are not because many of the series overlap. One clear case of disagreement concerns ion 217 reported by both "A" and "C" in LC4. Contractor C identified it as methyl naphthoquinoline, partly on the basis of the finding of quinoline and dimethyl quinoline and partly on the finding of other heterocyclic nitrogen compounds, carbazole, etc., in LC4. Contractor C stated that the signals were so weak for these compounds that, in fact, the identification depended heavily on the other inputs. Contractor A identified 217 as benzocarbazole largely on the basis of finding carbazole in the same sample. Interestingly, both "A" and "C" reported dibenzocarbazole at 267. Finally, in some cases, the nomenclature used by the contractors differed for the same series of compounds. For example, in LC5 "D" listed phenyl phenols C₁-C₄, MW 170-226, and "A" listed alkyl biphenyl-ols 170-240. Obviously these names refer to the same series, yet the usage of a different system of nomenclature is confusing.

TABLE 50. COMPOUNDS FOUND IN TAR SAMPLE BY GC/MS AND
REPORTED BY CONTRACTOR

Category	Compounds	Contractor			
		A	B	C	C
Fused alternate, nonalternate hydrocarbons	Naphthalene	---	---	---	---
	2-Methyl naphthalene	---	---	---	---
	1-Methyl naphthalene	---	---	---	---
	C ₂ -naphthalenes	---	---	---	---
	Biphenyl	---	---	---	---
	Acenaphthylene	---	---	---	---
	Acenaphthene	---	---	---	---
	Fluorene	---	---	---	---
	Phenanthrene	---	---	---	---
	Anthracene	---	---	---	---
	Fluoranthene	10	---	---	---
	Pyrene	10	---	---	---
	Benzo(a)fluorene	---	---	---	---
	Benzo(b)fluorene	---	---	---	---
	Benzo(a)anthracene	10	---	---	---
	Chrysene + triphenylene	10	---	---	---
	Benzo(b)fluoranthene	---	---	---	---
	Benzo(e)pyrene	10	---	---	---
	Benzo(a)pyrene	10	---	---	---
	Perylene	10	---	---	---
	Dibenzo(a,h)anthracene	---	---	---	---
	Indeno(1,2,3-Cd)pyrene	---	---	---	---
	Benzo(g,h,i)perylene	10	---	---	---
Heterocyclic sulfur compounds	Benzothiophene	---	---	10	---
Heterocyclic oxygen compounds	Dibenzofuran	100	---	---	---
Heterocyclic nitrogen compounds	Carbazole	100	---	100	100
	Benzidine	---	---	---	---
	Alkyl pyridines	---	---	---	100
	Quinoline	10	---	---	100
	Alkylquinolines	10	---	---	100
	Alkyl benzoquinolines	---	---	---	---
Phenols	Acridine	10	---	---	100
	Phenol	100	---	100	100
	Cresols	100	---	100	---
	Xylenols	100	100	100	---
	o-Isopropylphenols	---	---	10	---
	Trimethyl phenol	---	---	10	---
Number agreeing with GC data excluding fused alternate, nonalternate hydro- carbons		8	1	7	6

TABLE 51. LRMS SIGNAL ASSIGNMENTS FOR SELECTED COMPOUNDS REPORTED
BY CONTRACTORS IN THE COAL GASIFICATION TAR SAMPLE

Compound	MW	Contractor			
		A	B	C	D
LC4					
Carbazole	167	167	NA, P	167, 166, 139, 83.5, 69.5	167, P
Dibenzocarbazole	267	267	NA, P	63, 39, 267	NA, NP
Naphthol	144	144	NA, P	NA	144
LC5					
Methyl naphthol	158	158	NA, NP	158, 157, 115, 129, 128, 127	158
LC6					
Phenol	94	94	NA, P	94, 39, 66, 65	NA, P
Cresol	108	108	NA, P	108, 107, 77, 79 51, 39	NA, P
Ethyl/dimethyl phenol	122	122	122, 107, 94, 77	122, 107, 121, 39, 77, 51, 79	NA, P
Acridine	179	179	NA, P	NA, P	179
Quinoline	129	129	NA, P	NA, P	129
Pyridine	79	NA, P	NA, P	NA, P	79

NA = Not assigned.

NP = Not present in spectra.

P = Present in spectra.

6.3.2 Results and Comments from Specific Contractors

Each contractor's results will now be examined individually to pinpoint the interpretive processes used.

6.3.2.1 Contractor A Results of Tar Sample Analysis--

In the cases of the test spectra and test mixtures, one of the usual peak assignment rationales was to match peaks in the spectrum to a reference spectrum. In the tar sample fractions, however, this justification was not listed. Instead, other inputs were considered more useful in interpreting the spectra. The signal assignments were usually molecular ions for compounds and for members of a series associated with a compound. Fragment ions generally were not listed. All spectra were probe spectra. In fraction LC4, "A" reported primarily carbazoles and fused alternate-nonalternate hydrocarbons such as chrysene and pyrene.

The assignment rationale for carbazole was based on four factors:

1. The presence of an intense ion at m/e 167,
2. The vaporization or appearance of 167 at 100° C,
3. The proper LC fraction (4) for carbazole, and
4. The fact that carbazole is often reported as being present in coal tar.

The assignment rationale for benzocarbazole was similar to that given for carbazole:

1. Benzocarbazole (m/e 217) is often seen with carbazole and is often seen in coal tar in LC4.
2. The molecular ion vaporizes at 50°-100° C higher than carbazole.

Justification for the listing of alkyl carbazoles and alkyl benzocarbazoles was based on:

1. Finding the nuclear unit (carbazole, benzocarbazole),
2. Finding m/e values in a series successively 14 mass units higher than that of the nuclear unit,
3. Vaporization of each successive member of the series at successively higher temperatures, and
4. Decreasing abundance of series members with increasing number of carbon substitution; typically the first CH_3 substituent (e.g., methylcarbazole) is the most abundant.

The series of polynuclear aromatic hydrocarbons (fused alternate hydrocarbons) was justified on the basis of vaporization close together, but sequentially, near 200° C. The spectra shown were all taken at 70 eV and tend to bear out the assignment rationales given. In none of the cases above was the use of 15-eV spectra given as an aid to the interpretation.

In LC fraction 5, "A" reported alkyl series of biphenol-ols, fluorenes, dibenzofurans, and naphthenols. As expected, the assignment rationale was that homologous series spaced 14 m/e apart were found. Dibenzothiophene, a heterocyclic sulfur compound, was tentatively assigned. Both methyl and dimethyl benzothiophene were reported by "C" in this fraction. However, "A" states that, although there is a temptation with a sample of this origin to quickly assign a major m/e 184 ion as dibenzothiophene, several elements argue against that, which resulted in this assignment being dropped.

1. LC4 is the "usual" fraction for this compound.
2. The closely related compound naphthobenzothiophene is not present.
3. There are many comparable and related peaks that clearly are not thiophenes.

The assignment rationale for the alkylated series listed was that the 15 eV spectra clearly showed that there were several m/e 14-spaced series present, and abundant short aliphatic fragments from the 70-eV spectra supported the alkylation hypothesis. The general approach taken by "A" to identify such a series is to use the low voltage (15 eV) spectra to identify the nucleus of each series and then look for evidence to support the tentative identifications.

In this case, OH and C=O, indicated by IR, and also the LC fraction number are consistent with phenols and aromatic ketones. Compounds to be expected from a coal tar source are consistent with this. The homologous series idea is checked by observing the sequence of maxima for each component; each species in the series must maximize in a sequence directly related to the increasing molecular weight. Individual reference spectra are then compared to see if the spectrum of the unknown is consistent with the combined reference spectra of the series. However, this argument tends to contradict the rationale given earlier for the presence of alkylated carbazoles in LC4a. That rationale stated that there should be a decreasing

abundance of series members with the increasing number of the carbon substitution with the first CH_3 substituent (methyl-nucleus) being the most abundant. Yet in the probe spectra given for LC5, the 14 m/e series beginning with 170 biphenyl-ol shows increasing abundance with increasing CH_3 substitution up to 212 with 226 and 240 decreasing in abundance.

In LC fraction 6, phenols, acridines, quinolines, and fluorenones were the compounds most often listed. The assignment rationale for phenols was that a major ion at m/e 94 has a high probability in LC fraction 6 of being phenol. This tentative identification was supported by the presence of higher mass homologs at m/e 108, 122, and 136. The 15-eV spectra for this fraction confirmed this identification by showing just the parent ions with only a trace of the characteristic m/e 66 fragment. Phenol was also assigned a major concentration (more than its actual peak height might indicate) because most of it is lost in the probe vacuum lock during insertion.

Quinoline was identified on the basis of the sample and LC fraction content and on the strong m/e 129 ion that remains when the ionizing voltage is reduced from 70 eV to 15 eV. The identification of acridine was similar to that for quinoline. The naphthol and biphenylol series were identified by analogy and similarity to the spectra of LC fraction 5. Although not stated, it is assumed that the same rationale given for the other fractions was used to justify the homologous series thought to be present.

6.3.2.2 Contractor B Results of Tar Sample Analysis--

Contractor B analyzed all of the tar sample fractions using probe inlet at 70 eV. No compounds were reported for LC4 and 5 with the category aliphatic hydrocarbon reported. The signal assignments given were for ions at m/e 43, 57, and 71. The comment was made that in these samples no discernible molecular ion was available. In LC6, 3-ethyl phenol was listed based on the molecular ion 122 and three fragment ions 107, 94, and 77. If the contractor's spectra are examined, however, it becomes obvious that the failure to interpret the spectra and not the quality of the spectra was responsible for no identification being made. Several intense ions are apparent for these spectra taken over the probe heating cycle. Carbazole (m/e 167) and probably benzocarbazole are present in LC4 along with many ions above m/e 300. In LC5 a weaker spectrum was obtained but the one given only covers scans 53-76. LC6 shows the ethyl phenol ions as well as molecular ions for acridine (or benzoquinoline) and cresol.

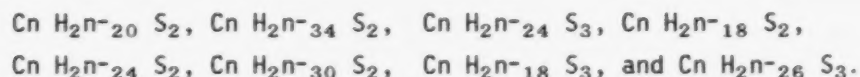
6.3.2.3 Contractor C Results of Tar Sample Analysis--

All fractions analyzed were run on both batch (120° C) and probe inlets (20°-300° C) and the data output consisted of oscillograph recorder traces.

Contractor C also reported some results for LC fraction 3. The mass spectrum of fraction 3 was run to aid in the interpretation of the later fractions. The mass spectrum of LC3 showed numerous PAH's; carryover of these compounds into LC4, 5, and 6 may account for the interference experienced in these fractions.

The more volatile compounds were seen when the sample was introduced through the reference inlet system (analogous to batch inlet) and fractionation of the less volatile compounds took place at various probe temperatures upon introduction through the direct evaporation inlet (analogous to probe inlet). At a probe temperature of 20° C the more common PAH's such as naphthalene (MW=128), acenaphthalene, fluorene, anthracene, pyrene, methylpyrene, chrysene, perylene, benzperylene, picene (MW=278), etc., were observed. At a probe temperature of 130° C the major peaks had shifted to the 250-350 molecular weight range. At 175° C the major peaks were in the 325-380 m/e range. The major peaks had shifted to the 370-480 m/e range at 240° C.

Some of the compounds, particularly at higher mass, might be attributed to compounds containing multiple sulfur atoms according to Lumpkin and Aczel (1977). These include the following series:



The mass spectrum of LC4 was characterized by peaks at almost every mass. The peaks that stood out above the background interference (possibly due to carryover from LC3) appeared to be carbazoles and other heterocyclic nitrogen compounds, primarily alkylated naphthaquinolines. The assignment rationales given for carbazole, methylcarbazole, and dimethyl or ethyl carbazole were that the most abundant peaks for these compounds were present and that LC4 was the proper LC fraction for carbazoles. At least five of the eight most abundant peaks were listed as signal m/e values for these compounds. Identifications of the other compounds listed were based on less firm evidence. Naphthoquinoline was assigned on the basis of a weak signal

at m/e 203, which prevented definite assignment, but naphthoquinoline was consistent with other heterocyclic nitrogen structures found in this fraction. The methylated homologs of methyl and dimethyl/ethyl naphthoquinoline at m/e 217 and 231 were justified similarly. Dibenzocarbazole (m/e 267) was justified on the basis of LC4 being the proper LC fraction for carbazoles. The probe mass spectra for LC4 support these identifications and indicate that most of the lower molecular weight compounds identified vaporized at a probe temperature of 20° C.

Contractor C found fraction LC5 to consist primarily of an alkylated series of naphthols, dibenzothiophenes, and possibly an aromatic nitrile. Phthalonitrile, methyl naphthol, dimethyl naphthol, and methyl dibenzothiophene were justified on the basis of the most abundant peaks being present in the spectra taken. No reference spectrum for trimethylnaphthol could be found but the structure was found to be consistent with others found in this fraction. Rationale for assigning dibenzothiophene and dimethyl dibenzothiophene were not given but are assumed to be similar to those given above. The probe spectrum for LC5 is consistent with these identifications.

Fraction LC6 was found to consist of an alkylated phenol series with the rationale given that the most abundant peaks for these compounds were present and that LC6 was the proper LC fraction for phenols. The phenol peaks were observed in a spectrum taken from the batch inlet analysis. However, upon examination of the probe inlet spectrum taken at 20° C, many other intense ions were observed that probably correspond to compounds often reported in LC6, such as acridine/benzoquinoline and quinolines. The presence of these compounds is consistent with the observations of "A" and "D" for LC6. These compounds were probably not listed due to an oversight on the part of the analyst.

6.3.2.4 Contractor D Results of Tar Sample Analysis--

According to "D", the tar samples exhibited a rather high level of background constituents that were mostly hydrocarbon in nature. Because of these background peaks, the use of low intensity fragment ions for positive identification of various species was precluded and only major fragment ions or molecular ions of significant intensity could be used in the interpretive process. All spectra were taken at 70 eV and run on probe inlet.

In all cases the LRMS spectra were interpreted using high mass molecular ion peaks. Characteristic peaks ($m/e \Delta = 14$ AMU) of homologous series were used to confirm the presence of a basic structure. For the most part, fragment ions were not present or were masked and could not be used in the interpretive process. Also, relative peak intensities were used from spectra taken over the probe heating cycle to determine if peaks were from the same compound or different compounds.

Comparison was made with IR data before the LRMS interpretation was finalized. In most cases correlations existed. The IR data did not positively identify species but did provide functional group information not present in the LRMS data. Using the functional group information, the LRMS data were refined.

There was one striking area of disagreement between the two techniques. In the tar fraction LC6, the IR data suggested significant intensity of acid species, none of which could be positively identified from the LRMS data.

Contractor D reported alkylated series of pyridines, carbazoles, and naphthols in LC4 based on the rationale given above. Upon examination, the probe spectrum for LC4 indicated that the analyst also considered the possibility of a homologous indole series.

Phenols, naphthols, benzophenones, and anthraquinones were reported in LC5. The assignment rationale was that once phenol was identified (m/e 94), several substituted patterns were evident. Only species yielding strong molecular ions were detected. Fragment ions, indicative of functionability, would be lost in the baseline peaks that are typical of most Level 1 samples. As a general rule, only strong molecular ion species were identified.

Acridines, quinolines, and pyridines were reported in LC6 although the pyridine peaks were suspected of belonging to phenols. Suspected molecular ions were the only mechanism for compound identification. Patterns of these molecular ions (spaced at 14 m/e units) helped in their identification. Many compounds, totally different in structure and having the same molecular weight, could not be distinguished using this procedure.

6.3.2.5 Conclusions--

Several differences in the contractors' interpretations of the tar sample and the synthetic samples were observed. In the tar sample interpretations, the finding of a homologous series was almost essential to the

identification of compounds whereas in the cases of the synthetic samples there were few if any homologous series present and thus the analysts had to look elsewhere for information, typically reference spectra like the Eight Peak Index or NIH/EPA Data Base. All contractors depended heavily on finding molecular ions of parent nuclei before using this information to identify homologous series. Only "A" used low ionizing voltage to aid in identifying molecular ions. Other contractors assumed that the 70-eV spectra provided sufficient information. Only "C" reported using batch inlet data to identify compounds, i.e., phenols in LC6, although many of these ions were also present in the 20° C probe spectra for this fraction. One possible bias inherent in a sample such as a coal gasification tar sample and manifest in many of the assignment rationales given is that most experienced LRMS analysts doing EA work have seen and analyzed tar samples before and thus have predetermined opinions about what should be in the sample. Obviously this is a two-edged sword because familiarity with a sample and its source can aid in anticipating the type of chemistry involved and the potential reaction products produced. However, it can also "blind" the analyst to the discovery of "unexpected" compounds. This did not appear to be a significant problem for the tar sample in this study although it is a valid concern.

6.4 CONTRACTOR COMMENTS AND APPROACHES TO INTERPRETATION OF LRMS SPECTRA

To gain a fuller understanding of the interpretive process and to clarify several of the interpretations, the LRMS analysts for each of the four contractors were contacted. Three areas were discussed:

1. Their results on the test spectra, mixtures, and tar sample;
2. Specific comments they made in their reports;
3. Spectral interpretation in general.

In addition, three out of the four laboratories were visited and additional information was obtained along with the contractors' recommendations regarding the usefulness of this study and how best to disseminate useful information gained from the study.

6.4.1 Contractor A Comments

6.4.1.1 Test Spectra and Mixtures--

The mass spectroscopist for Contractor A had no additional comments regarding the test spectra and mixtures other than that he had not seen the

fused ring acids (fluorene carboxylic acid and fluorenone in carboxylic acid) previously, although after reviewing the IR results he was able to identify both of them in mixture LC6 based on the loss of the characteristic carboxylic acid fragments of 45 and 17 m/e.

6.4.1.2 Report Comments--

The analyst was asked the following questions regarding the results reported for the analysis of the test spectra and mixtures.

1. In the spectral interpretation test spectrum LC6b, the LRMS assignment was for hydroxyanthraquinone; in test mixture LC6 it was originally the same but was changed to acids (fluorenone carboxylic acid) after seeing the IR results. Why was the LRMS interpretation changed in the case of LC6 even though both IR spectra LC6b and LC6 are nearly the same?

In the case of the test spectra, the LRMS and IR results were prepared independently. The LRMS results were submitted for inclusion in the report prior to the generation of the IR spectra. The IR analyst reviewed the LRMS results, which indicated hydroxyanthraquinone as the major species present, and, based on this evidence and the IR data, verified hydroxyanthraquinone as being present. At no time did the IR and LRMS analysts consult with one another on the interpretation of the test spectra. Again, in the case of the test mixtures, the analysts prepared their reports independently but this time the analysts worked more closely together after the initial observations were made. It was because of this interaction that the results for LC6 were revised. Initially, IR reported carboxylic acids and LRMS reported hydroxyanthraquinone, both prior to seeing each other's reports. Then, after reviewing each other's results, the mass spectra were reexamined and the fused ring acids discovered.

This is a clear example of how the interaction of IR and LRMS can provide a more accurate picture of a sample.

2. Referring again to the interaction of IR and LRMS, anthrone was missed in the spectral interpretation test by LRMS but was correctly identified by LRMS in test mixture LC5 prior to seeing the

IR results. After the IR was reviewed, anthrone was dropped in favor of an "aldehyde." Why was the change made?

Anthrone was dropped because the IR analyst could not find a reference spectrum for anthrone (and thus could not verify the LRMS observation) and on the basis of only two LRMS peaks, 193 and 194, it was dropped in favor of the more plausible "aldehyde." This is an example of how IR data or, more correctly, the absence of a suitable IR reference spectrum, led to dropping a compound that was actually present.

3. Based on the findings concerning the interaction of IR and LRMS discussed in 1 and 2, it was stated in the Contractor A's report that new categories identified by IR but not LRMS might be given 100 intensity ratings. The mass spectroscopist was asked to comment on this.

If a conflict arises between the IR and LRMS interpretations that cannot be resolved by reference spectra companions, then probably such categories should be so listed. However, this should be a minor problem.

4. In the spectral interpretation test comments, the assignment rationale sometimes given was to "match prominent peaks to reference spectra and thereby make as complete an accounting of the spectrum as possible." What kind of reference spectra are generally used in the interpretation?

The answer to this question will be more fully developed later in this discussion, but, briefly, the Eight Peak Index and the NIH/EPA data base are most often used.

5. When looking for a homologous series in a mixture, isn't it possible that if the analyst errs in assigning the parent compound, the other assignments will be wrong as well?

Other inputs should clue the analyst that he is wrong. Also, fragments from the homologous series should vaporize in a regular sequence with the heaviest coming off last.

6.4.2 Contractor B Comments

The analyst stated that these samples and spectra were among the first Level 1 samples he had ever run and that no one briefed him on the objectives

of the round-robin study. He stated that his previous mass spectrometry experience, approximately 10 years, was in the area of analysis of biological materials. The analyst stated that he had never seen the spectrum of aromatic hydrocarbons prior to these samples. Upon reviewing the results with the analyst, he pointed out that several of the compounds that were missed were listed in his notes, but were inadvertently omitted from the report; for example, methyl pyrene/benzofluorene. Several other compounds (naphthalenes) were noted by him on the spectra but also were not listed in the report. He stated that he could not see how the other contractors were able to identify compounds like the indoles or phenols in the spectra without having had extensive experience in interpreting similar spectra. Several questions concerning the reporting of the test results were also asked.

1. Why weren't both sets of forms completed for both the test spectra and mixtures?

The analyst did not know because he did not write the report.

2. Although in the spectral interpretation test report the analyst checked the box marked "pattern of peaks," usually only 1 peak per compound identified was listed. Were other peaks used to make compound/category assignments?

Other ions were looked for in certain cases but, in general, the eight most abundant ions for a compound were not looked for in the spectra. All significations above a certain level of intensity were considered, not just the eight most abundant. The analyst did say that in the future he will pay more attention to even-mass, non-nitrogen-containing ions as well as look for lower mass ions as possible molecular ions and fragments. Also, he would like to see the IR results beforehand.

3. The report states that "B" believes that LRMS is better for analyzing for fused ring aromatics than is IR and vice versa for highly polar compounds. Why do you believe this to be so?

The analyst responded by stating that he did not write the report and therefore could not comment on those statements.

6.4.3 Contractor C Comments

All comments regarding Contractor C results will appear later in this discussion.

6.4.4 Contractor D Comments

1. The analyst suggested that metastable ions are a potential aid to interpretation. How can they be so used?

When there are two to three components in a mixture, "lumps" in the baseline spectra will appear due to diffuse metastable ions. The ions can be used to correlate mass peaks with one another. However, they are only visible on oscillograph traces because the data system removes them.

2. The analyst noted earlier (p. 168) that introduction of large samples via direct probe on his instruments can result in an enhancement of molecular ion peaks by +1 unit. What is occurring here and how can this be avoided?

When there is excess sample in the ion sources, gas in the source will exchange protons with some of the sample ions. The result of this process is the displacement, by one mass unit, to a higher mass for molecular ions. If this is not taken into consideration by examining spectra over a heating profile where varying concentrations of sample are passing to the ion source, one could easily confuse a hydrocarbon compound having an even molecular weight with a nitrogen-containing compound with an odd molecular weight one mass unit higher. This did not occur with the test mixtures and tar samples because the sample concentration was purposely kept down.

3. Were any of the test mixtures and tar LC fractions run by batch inlet as well as probe?

The batch inlet was not used due to malfunction of the LRMS instrument at the time the samples were being analyzed. For regular Level 1 work, though, the batch inlet is used.

6.4.5 Contractors' Responses to General Questions

In addition to questions regarding specific comments the contractors made in their reports, all four analysts were asked to respond to a series of general questions designed to define more clearly and in detail (1) the exact approach they use to interpret spectra, (2) their opinions regarding variations on these approaches, and (3) how best to disseminate the information needed to perform spectral interpretation.

Each analyst was asked to give a step-by-step description of how he interprets low resolution mass spectra.

6.4.5.1 Contractor A--

Contractor A is concurrently writing a guidelines document for the interpretation of Level 1 low resolution mass spectra. The following is not intended to adequately summarize this document; however, it does give an overview of the approach the "A" analyst uses to interpret spectra.

Once the spectra are generated, the analyst looks for at least two to three peaks that seem to be connected by their coelution from the LC or covaporization during the probe heating cycle. The analyst then goes to the Eight Peak Index to see if the other five or six most abundant peaks are present. The analyst feels that at least two or three peaks are needed to narrow down the list of possibilities because typically there are dozens of potential compounds listed having the same molecular ion but far fewer sharing two or three ions. Another input to the interpretation obtained from the spectra themselves is that the peak intensity ratios for peaks suspected of belonging to the same compound cannot be smaller than expected on the basis of the ratios given in the Eight Peak Index. If they are larger, then this often means that fragment ions from other components are contributing to the intensities of the ions being studied. For example, "A" could not justify fluorene in either test spectra LC5a or test mixture LC5 due to the majority of its eight most abundant peaks also being common to those of other more easily identified compounds present in the spectra obtained. Molecular ions are more easily found by analyzing the sample at low ionizing voltage (15 eV). At 15 eV, most fragment ions are absent. By comparing the ions remaining at 15 eV with those also present at 70 eV at the same probe temperature, the molecular ions are thus distinguished. Another important clue already discussed in the other sections of this report is the presence of a homologous alkylated series distinguished by molecular ions at 14 m/e intervals with the methyl (C_1) substituted species usually the most significant member of the series. The other inputs the analyst often relies upon are the IR data (previously discussed) and the LC fraction a suspected compound elutes in. Until recently, the analyst used the LC fraction Table 17 in the Level 1 Manual to accept or reject certain compounds on the basis of their expected LC fraction and the actual fraction

they eluted in. Now the table will be used less to rule out compounds but still used to verify their presence. The sample source is also an important input along with any baseline data collected on the sample. In general, then, the inputs "A" uses to interpret mass spectra are as follows.

1. The mass spectrum itself (actually a series of scans taken over a range of temperatures and at varying ionizing voltages)
 - a. probe temperature
 - b. ionizing voltage
 - c. homologous series
 - d. intensity ratios
 - e. compound- or category-specific descriptors (e.g., nitrogen-containing compounds usually have odd molecular weights)
2. IR data
3. LC data--carryover from previous fractions
4. Sample source

6.4.5.2 Contractor B--

The analyst runs all samples at 70 eV and direct probe programmed from ambient to 350° C at 40-50° C/minute. Only intense ions are looked at and those that can be identified as molecular ions or major fragment ions are checked against reference spectra in the Eight Peak Indices, the EPA/NIH Data Base, and the American Petroleum Institute Index of Mass Spectra.

6.4.5.3 Contractor C--

In general, when the analyst sees a spectrum, he looks for the highest m/e peak, assumes it to be a potential molecular ion and then proceeds to look for "logical" fragment ions. An intensity and m/e criterion is set below which no ions are looked at. Usually this covers any ions below 5 to 10 percent intensity relative to the most intense ion and also those below m/e 30.

The intensities of the peaks thought to belong to halogen-containing species are also looked for. The intensity of the suspected molecular ion will often clue the analyst as to the type category present in the spectra of the mixture. For example, aromatic compounds, especially fused-ring aromatic compounds typically have intense molecular ions and aliphatic hydrocarbons do not. If at this point the analyst has narrowed down the list of possibilities to 5 to 10 compounds, the IR analyst is consulted and

these 5 to 10 are reduced to 2 or 3 or sometimes 1 compound. The IR analyst has already interpreted the IR spectra of the LC fraction studied prior to consultations with the mass spectroscopists so as not to bias the interpretation. The IR analyst then obtains reference spectra of the compounds suggested by the LRMS and tries to match reference spectral bonds to those in the generated spectra. Sometimes the IR analyst will run his own spectra of the suspected compound and compare it to the unknown spectra. If the IR analyst's pre-LRMS generated interpretation doesn't agree with the LRMS, it is noted as being so. Relative intensities are assigned to the peaks of interest. Once a peak is assumed to be a molecular ion, the analyst immediately goes to the Eight Peak Index and searches for each of the remaining seven fragment ions in the spectra. Each fragment that is identified as belonging to the molecular ion is labeled as such. After the compound and its fragments are so identified, the analyst proceeds to the next high mass ion and so forth from higher to lower masses until all ions in the spectra that meet the intensity and m/e criteria are accounted for. The presence of doubly charged ions is especially useful in identifying fused-ring compounds. If most of the eight peaks are not found to be present, then these compounds can be eliminated. The analyst does not rely on the relative intensities for peaks given in the Eight Peak Index and consequently does not attempt to take ratios of peak intensities in the spectra because these vary greatly for many compounds depending on the instrumental conditions used to obtain the spectra. However, a "pattern" of relative intensities among the eight peaks is sometimes looked for.

Other inputs can be significant to the interpretation process but are often not as dependable sources of information as the spectra themselves. Low ionizing voltage is never used to simplify spectra. Variable probe temperature is useful to the analyst. The appearance and disappearance of ions is used to link them together. The LC fraction number being studied may be helpful but is often undependable. The analyst uses it primarily to verify compounds suspected of being present. It is never used to rule out the presence of any compound. Thus the LC fraction number is only of secondary importance to the interpretation. The analyst finds that homologous series inputs are not that essential to compound identification. However, when present, as was the case with the tar sample, they are easily recognized

and can assist in the interpretation although their absence, he feels, does not hinder the interpretation.

6.4.5.4 Contractor D--

The Contractor D analyst's approach to mass spectral interpretation is to pick intense, high, even-mass ions and look for fragments that could be from the selected high-mass ion. Then a standard reference book, the Mass Spectral Correlation Tables or the Eight Peak Index, is consulted and the molecular weight region being studied is searched for compounds that satisfy the analyst's observations about the molecular and fragment ions. Without apparent molecular ions, he has difficulty identifying and relating fragment ion spectra and thus difficulty identifying the categories and compounds present. As stated earlier in this report, the analyst finds that the presence of homologous alkylated series of compounds facilitates the interpretation. Compounds such as fluorene- and fluorenone-carboxylic acid that are not listed in his reference book are most difficult to identify. The contractor feels that odd-number molecular ion species should be attributed to N-containing compounds. He also looks for C^{13} isotope peaks. He finds the IR does not complement the LRMS a great deal. Rather, it expands the possibilities of compounds present. However, he feels that this sometimes leads to false identifications being made. All analyses are performed at 70 eV due to the nature of the instrument used. The GC/MS instruments "D" uses to do Level 1 LRMS require refocusing the source after each eV switch, therefore the analysis has to be performed at either 15 eV or 70 eV, but not at both unless the analyst is willing to accept inconsistent results. The use of variable probe temperatures over a heating cycle is useful to the analyst because sample quantities gradually decrease over the course of the cycle and thus depletion of several peaks simultaneously could indicate that they are related. Also, if these peaks are related, the peak relative intensities should stay constant over the course of the heating cycle during which they are vaporizing. The expected LC fraction table in the Level 1 Manual is used extensively, with a ± 1 LC fraction window of acceptability, as is the knowledge of the source being studied. The analyst does not try to account for the presence of all ions above a certain intensity.

A comparison of some of the factors contributing to the contractors' interpretations as shown in Table 19 suggests some agreement as to the value

of most of the inputs listed. However, the application of these data inputs to the study spectra and samples deviated considerably from the Table 19 inputs, especially for contractors B and D. It was also quite clear that at least until this study, the IR was not given equal weight with the LRMS with "B" giving it more weight and the others less than LRMS.

What follows are the analysts' responses to more general questions dealing with the utility of specific inputs identified as being useful to LRMS interpretation and the analysts' views on disseminating this information.

6.4.6 Contractors' Responses to Questions Regarding Generation of LRMS Spectra

6.4.6.1 Question #1--

What kind of data output do you find more easily interpretable?

- a. Computer-generated (digital)--all peak intensities relative to the base peak, which is arbitrarily assigned an intensity of 100; or
- b. Oscillographic trace analog recordings.

• Contractor A

There are unique advantages and disadvantages to both methods but overall there is a net balance in favor of the data system. The advantages of the computer-generated peaks are that it is easier to make decisions regarding the vaporization of certain peaks. An entire run or several scans from the run can be integrated, whereas with the manual system a great deal of paper is generated in a very time-consuming process. It is difficult to relate one scan directly to one or more preceding/succeeding scans. The advantage of the oscillographic traces is that individual peaks within a scan are more easily associated with one another due to the availability of multiple sensitivity and the size of the scale used. Computer printouts are often jammed together. Also, the computer removes metastable ion peaks that are present in oscillographic traces. The analyst noted that for this report the computer-generated scans were reduced both in size and in number to show representative scans. "A" only recently switched from using the oscillographic trace to the data system output. The analyst does not feel, though, that the main use of the computer data system is to automate the process. Whether manual or computer printout is used, he prefers to monitor the operation so as to maximize the information achieved by varying the conditions (probe temperature, eV) as the analysis proceeds.

• Contractor B

The analyst prefers the computer-generated spectra, stating that without it there would be too much information generated by the quadrupole mass spectrometer for the oscillograph to plot. Also,

the computer-generated spectrum for a sample is preferred for the purpose of presenting a composite spectrum to include all the information given by the sample during the entire volatilization process.

- Contractor C

The analyst obtains all spectra via the oscillographic trace record. The oscillographic trace is performed at four sensitivities simultaneously and the mass scale is listed at the bottom of each spectrum. Although the analyst was not familiar with computerized printouts of mass spectral scans, he did cite some of the potential advantages and disadvantages of both such systems. While the computer does assign peak m/e to certain peaks it usually does so only at integral masses. Sometimes the computer rounds off fractional masses to the nearest integral mass. This, of course, can be misleading to the analyst who often needs the confirmation of the presence of doubly charged ions at half masses to justify the interpretations. Also, the computer printouts are typically squeezed together in a small space so that peaks are sometimes crowded so close together that they cannot be differentiated. The oscillographic trace, while not providing any real increase in resolution over the computerized printout is a more expanded version. The analyst especially likes the oscillographic trace because intense doubly charged ions at half masses characteristic of fused ring systems (for example, 89.5--anthracene, phenanthrene) are more easily discernible and accurately attributable to a given m/e .

- Contractor D

In regard to the comparison of oscillographic trace recordings vs. data system outputs, the analyst says that the resolution of the data system output is very much instrument-dependent. For example, "A's" mass spectrometer has a greater resolving power than "D's" quadrupole instruments whose data system cannot separate half mass peaks or other peaks at nonintegral m/e values. Instead it shows them as peaks on either side of the correct m/e designation. Sometimes major peaks are shifted. Thus, doubly charged ions are missed by quadrupole instruments. However, the analyst doesn't feel that doubly charged ions are important interpretation aids for the analysis of Level 1 data. The analyst still favors the data system output over the oscillographic trace due to easier availability of the data. Also, the oscillographic trace mass/charge scale must be marked by hand, which can be time consuming. However, he feels it is easier to see intensity relationships among peaks by the trace method because, in general, there is one spectrum present at four intensities on the same sheet of paper. Another advantage of the data system is that the scales can be expanded both horizontally and vertically.

6.4.6.2 Question #2--

In the computerized printout of mass spectral scans, the computer sometimes prints m/e values above certain peaks. Why does it do this? Also, in

this same regard, why do some computer-generated m/e scales not always agree with the m/e values assigned by the computer to certain masses?

- Contractor A
There are problems with rounding off errors by the data system. Some distortion is experienced with the INCOS data system "A" uses. This is just something the analyst must be aware of and learn by experience with the instrument and data system used.
- Contractor B
"B" was not asked this question.
- Contractor C
Refer to "C's" response to question 1.
- Contractor D
Typically, the data system has been instructed to print the mass above the largest peak in a region but all peaks can be treated thusly if desired.

6.4.7 Contractors' Responses to Questions Regarding Interpretation of LRMS Spectra

6.4.7.1 Question #1--

Is there a systematic approach to the use of variable probe temperatures and ionizing voltages or does the analyst have to treat each sample in a unique fashion?

- Contractor A
The analyst typically only gets to run the sample one time. The probe cycle goes from 60° to 90° C source temperature up to 300° to 400° C over the course of 15 to 30 min. A scan is typically taken every 5° to 10° C. The sample is usually at a lower temperature than the source. Variations in the ionizing voltage are a matter of the analyst responding to the nature of the sample. For example, if a sample is highly aliphatic it should be run at 70 eV only. Simple fused-ring compounds should just be run at 70 eV with an occasional check at 15 eV. Other compounds including substituted fused rings should be run at both 15 and 70 eV, although the exact breakdown will vary from sample to sample.
- Contractor B
As stated earlier, the probe runs are programmed from ambient to 350° C at 40° to 50° C/min. All scans are made at 70 eV, although the analyst does think that some scans taken at 15 eV might provide useful information.
- Contractor C
Probe runs are made over the temperature range 20° to 300° C by increasing the probe temperature 50° C after each scan. In the

case of synthetic mixtures LC5 and LC6, molecular ions and identifiable fragments for all compounds identified were found in the 20° and 120° C spectra for these mixtures. Spectra taken at other temperatures did not disclose the presence of new molecular ions and hence no new compounds, although the observed depletion rates did give an indication of the concentration of the species present. However, in the case of the coal tar, the spectra obtained at different temperatures did provide evidence of new molecular ions appearing with increasing temperature. For example, in fraction LC3 the simple fused-ring compounds, anthracene, chrysene, etc., vaporized at 20° C; other heavier species did not appear until higher temperatures were reached. The ionizing voltage is always 70 eV. Spectra are never taken at 15 eV.

- Contractor D

Probe runs are temperature-programmed over the range 20° to 300° C. The spectra obtained are compared to see if the relative intensities for certain peaks stay constant over a range of temperatures. If several peaks exhibit this common behavior then there is a good possibility that they belong to the same compound. The appearance of new ions as the temperature increases can also signify the presence of new molecular ions. As stated earlier, the GC/MS instruments used by "D" are not suited to switching from 70 eV to 15 eV and vice versa within a series of scans because the source has to be refocused after each switch. One alternative procedure that could be used with this particular instrumentation to obtain molecular ion information similar to that obtained at 15 eV is chemical ionization mass spectrometry. The instrument can easily be switched from EI (70 eV) to CI during the probe cycle.

6.4.7.2 Question #2--

With regard to the Contractor D's suggestion that CI be an alternative to 15 eV spectra, what are the particular advantages and disadvantages of CI?

- Contractor A

Chemical ionization should only be an approved alternative if it is proven to be both time and cost efficient. Also, as is the case with 15 eV spectra there is no reference library of CI spectra readily available. Analysts will probably have to generate their own CI and/or 15 eV spectra.

- Contractor B

In analyzing these samples by chemical ionization, little more information is attainable than by electron impact. In a real sample analysis situation, prior knowledge on what information CI can provide cannot be established.

6.4.7.3 Question #3--

What is the minimum amount of information needed to identify categories/compounds in a mixture?

- Contractor A
The interpretation process is highly iterative and requires consistent inputs from the IR, the sample source, LRMS, and the LC fractionation to adequately make such a decision.
- Contractor C
The presence of three to four characteristic peaks is sufficient information to identify categories and sometimes even compounds in a mixture.

6.4.7.4 Question #4--

How useful are the non-LRMS inputs of IR, LC, and sample source to the interpretation process and how are they used?

- Contractor A
Prior to this study, the IR and LRMS reports were prepared independently with little or no interaction between the analysts. A third party made the Level 1 summary table compound/category assignments based on a review of both sets of data. Based, in part, on the results of this study, though, the IR and LRMS analysts agree that several iterations between the IR and LRMS analysts would be useful in resolving conflicts as well as in verifying observations. Also, the IR has been shown to be useful in identifying categories not immediately obvious to the LRMS analyst. An example is the case of the fused-ring carboxylic acids in test mixture LC6 that were originally not identified by LRMS. However, after consultation with the IR analyst who reported carboxylic acids in the IR spectra, the LRMS analyst was able to go back, reinterpret the spectra, and identify not only the category acids but the individual compounds as well.

The significance of the LC fraction as an interpretation input has also been questioned as a result of this study. Previously "A" used the LC fraction in which a suspected compound was appearing as a criterion on which to both exclude and verify the compound's presence within ± 1 LC fraction of the "expected" based on Table 17, p. 152, of the Level 1 Manual. An example of the LC fraction criterion being applied was in the case of test spectra LC5a in which the analyst correctly found m/e 216 as a molecular ion for methylpyrene (benzofluorene is the correct choice) but could not justify its presence in LC5a because it was two fractions too late for a fused alternate, nonalternate hydrocarbon according to the Level 1 Manual. Again, in test mixture LC5, methylpyrene was reported and although the lateness of the LC fraction was again used as evidence for excluding the compound, the compound was listed on the basis of a strong confirmatory match of peaks that covaporized together at 150° C. "A" has done more work on delineating the extent of spreading of categories and compounds over LC fractions. In this latest work, the range over which individual categories can be expected to elute is as great as three to four fractions. It is not impossible for compounds from one category to be observed to elute over as many as four LC fractions. However,

the majority of the compounds from this category should still be observed in the correct LC fraction. Also, individual compounds in general should elute within ± 1 fraction of the expected. Usually, if an individual compound is observed in more than three LC fractions, i.e., the expected and those on either side, then either the compound identification is wrong or the LC separation is unsatisfactory. The only case where such an elution would be expected is if the great majority of the sample loaded onto the column is one compound (e.g., 50 mg of anthracene). Needless to say, this seldom occurs in real assessment samples. Although the LC separation data are generally very useful for delineating the presence of individual compounds, the data should still be used with caution in evaluating the presence or absence of compound classes. The sample source is still considered an important input. Specifically, the analyst should be aware of the type of chemical processes occurring in the source and should be aware of potential compounds and categories thought or known to be associated with the process although under no circumstances should these "expected" compounds be used to bias the interpretation.

- Contractor B

Other inputs can be valuable to help differentiate between compounds giving similar spectra.

- Contractor C

In general, the LRMS analyst interprets the mass spectra and generates a list of several compounds that could correspond to each set of molecular ions and fragments identified. The IR analyst has also interpreted the IR spectra before seeing the LRMS. The IR analyst then using the IR interpretations generated and the initial LRMS compounds identified searches the DMS (Documentation of Molecular Spectroscopy, Butterworths and Verlag Chemie) reference file for these compounds. Sometimes the LRMS observations cannot be verified and, in these cases, the IR analyst suggests alternative ones. Several iterations usually occur before the final assignments are made. One example of how the IR was used to change the LRMS interpretation was the case of fluorenone in test mixture 6. LRMS initially indicated perinaphthenone. However, the IR spectrum did not compare well with the reference spectrum for perinaphthenone. As a result, the IR analyst suggested fluorenone and the LRMS data were rechecked for fluorenone. A better match was found. The IR data are also used to semiquantitate the presence of compounds once they are identified. The LC fraction a compound elutes in is not considered a significant input and is not used to exclude compounds. For example, in the test spectra LC4a-LC5b, the analyst indicated that although it seemed a little strange that fused alternate, nonalternate hydrocarbons would be appearing in LC4 and 5, this did in no way hinder the interpretation. However, the LC fraction can provide confirmatory evidence if the other inputs agree. The sample source is not considered an important input.

- Contractor D
The IR data are used to help confirm the LRMS findings. However, if there is a conflict between the two, both categories thought to be present are listed. The expected LC fraction ± 1 is used extensively to narrow down the possible categories and compounds present. The interpretation is also much easier if the sample source has been well characterized and a list of possible compounds/categories expected to be present has been generated.

6.4.7.5 Question #5--

What references are frequently employed to aid in the interpretation of mass spectra?

- Contractor A
The tabulated Eight Peak Index of Mass Spectra is frequently used because of the large number of compounds listed and because it is organized with respect to molecular ions and fragments. The EPA/NIH Data Base is also used quite frequently. The API (American Petroleum Institute) Index of Selected Mass Spectral Data was used a great deal in the past but is somewhat limited in scope. Three other references used more as guides to interpretation are Reed's Applications of Mass Spectrometry to Organic Chemistry, Budzikiewicz's Mass Spectrometry of Organic Compounds, and McLafferty's Interpretation of Mass Spectra, 2nd edition.
- Contractor B
Essentially the same references used by "A" are used.
- Contractor C
The analyst relies primarily on the Eight Peak Index to verify and assist in the interpretation. When more than one reference spectra is given for a compound, the analyst looks for consistency in the ones reported. Usually there are only subtle differences. The analyst has found this reference to be generally reliable, although one example from test mixture 6 revealed an error in the Eight Peak Index. The compound 2-methyl-1,4-naphthaquinone has a listed molecular ion of 172 at an intensity of 0.00. However the analyst noted and the spectra from Contractors A and B verify that this is inconsistent with the compound's structure. A much more intense ion at 172 is expected and was observed. So the analyst recommends that in using the Eight Peak Index, one should also use good judgment and not blindly accept the listings as is. The analyst finds that the EPA/NIH Data Base is full of errors. For example, the mass spectrum of a compound with 15 chlorine substituents has no chlorine-containing peaks present anywhere in the entire spectrum.
- Contractor D
The analyst's primary source of information besides the Eight Peak Index is the Mass Spectral Correlation Tables by McLafferty. This is a compendium of mass numbers and all plausible fragments from a given mass number. It is frequently used by the analyst to tell

if one peak can logically come from another. The correlations table usually will not disclose the structure of a molecular ion. This reference source is somewhat limited in scope in that only low-mass compounds are listed. The Eight Peak Index is used occasionally if an unusual ion is observed to be present. The analyst finds the Eight Peak Index generally useless for low mass peaks. An example of a case where this index would be used is if phthalate esters were suspected by way of a prominent 149 peak. In general, though, experience is used more often than any of the reference lists to interpret spectra. Also, the analyst does not try to account for all ions below a certain intensity or m/e value. Instead, higher mass ions, regardless of their intensity, are considered significant and are studied and lower mass ions at low intensities are generally ignored. The rationale for this approach is that the high mass ions are probably molecular ions or prominent fragments of molecular ions and the low mass ions may be insignificant fragments and/or part of the background spectra. One final qualification to the use of reference indices is that one must be very careful in using the m/e and intensity values shown because the spectra were probably obtained under instrumental conditions somewhat different than the analyst's laboratory is using. For example, spectra obtained on a quadrupole instrument will differ from those obtained on instruments using other ion separation systems.

6.4.7.6 Question #6--

How much time did it take to interpret the LRMS spectra in this study and, in general, how long does it take to interpret "real" Level 1 EA spectra?

- Contractor A
To interpret the test spectra, 1 to 2 hr was spent on each spectrum; for the test mixtures slightly more than 2 hr was used to run the sample and interpret the data generated. Two hours is also the amount of time generally allotted for running and interpreting real EA samples. These estimates do not include interaction with the IR analyst. Typically, all seven LC fractions for a sample are run consecutively prior to doing any interpretation. This tends to speed the interpretation because the analyst can now use many clues, such as comparing peak intensity ratios from LC fractions, etc.
- Contractor B
Approximately 30 min to 1 hr were spent on spectral interpretation including consultation with the IR analyst. As a result of this study, the analyst will, in the future, look more closely at the data and want to see the IR data first. Thus more interpretation time per sample is anticipated.
- Contractor C
The interpretation of each test spectrum took approximately 1 day (8 hr) per spectrum excluding consultation with the IR analyst; the analysis of the test mixture and spectra took only ½ day for

each. The time normally taken to analyze real EA samples is about $\frac{1}{2}$ day per LC fraction.

- Contractor D
The analyst normally spends 1 hr per LC fraction with the interpretation of the first fraction always the most difficult. Much more effort was put into interpreting the spectra from this study. In general, the analyst should not spend more than a couple of hours interpreting the spectra lest the effort become non-cost-effective.

6.4.7.7 Question #7--

How much training does a chemist need to be able to interpret Level 1 LRMS data?

- Contractor A
Several weeks to a month should be sufficient time to teach a chemist who can already successfully interpret and identify pure compound mass spectra. It depends heavily on who the teacher is. This particular analyst has over 20 years' experience as a mass spectroscopist.
- Contractor B
Although new to EA work, the analyst recommends a background in mass spectrometry as well as several years of experience with EA data. The analyst has 10 years' experience as a mass spectroscopist.
- Contractor C
The analyst feels that the successful mass spectroscopist should have several years' experience and be able to identify molecular ions. This analyst has 12 years' experience as a mass spectroscopist.
- Contractor D
The analyst recommends that the mass spectroscopist should have at least an MS degree or the equivalent in experience. This person should possess an understanding of the theory of mass spectrometry as well as have 2 years' experience interpreting data from a number of EA sources.

6.4.7.8 Question #8--

One potential problem area concerns the reporting of categories for multifunctional group molecules like fluorenone carboxylic acid. Some contractors listed it as an acid, some as a ketone. It is both. How should it be listed?

- Contractor A
To satisfy the requirements of Level 1, both categories should be listed because both are potentially of significance to health. The quantitation of such categories is and should be the subject of further investigation.

6.4.7.9 Dissemination of Information--

Several of the contractors were also asked to suggest ways to disseminate the information gained from this study other than the final report itself. The "D" analyst suggested that a conference be held with the mass spectrocopists from each major EA contractor present. He feels that it should be limited to 8 to 10 people at the most. Also, a guidelines document would be useful for inexperienced analysts. However, he feels that such a document would not alter the approaches taken by the experienced analysts. Contractor A feels that a workshop/ conference is also potentially a useful vehicle for increasing the level of awareness of Level 1 LRMS analysts. "A" is also preparing a guidelines document for LRMS analysts. Several example spectra are interpreted in this document. In conjunction with this document, both "A" and RTI feel that a set of completely worked out spectra plus a set of training spectra would be useful to analysts interested in improving their state of awareness.

6.4.8 Summary

It is obvious from the results of this study that there is a great disparity in not only the results achieved by the contractors but also in the approaches used to generate these results. In general, the "A" and "C" analysts appear to be more successful at identifying compounds and categories for two reasons. Both use systematic, if somewhat different, approaches to interpreting the low resolution mass spectra obtained. Both set criteria as to the m/e range and intensities of peaks to be accounted. Both rely heavily upon the Eight Peak Index of Mass Spectra to assist them in their interpretations. One possible criticism of their approach is that perhaps too much time is spent on each LC fraction's spectra and that it is not cost effective to try to analyze and interpret a large number of samples by their approaches. This contention cannot be answered by this study.

Even if a laboratory finds it impossible to modify all of its interpretation procedures to include all of the methods used by "A" and "C", some of them can and certainly should be adopted.

SECTION 7

CONCURRENT UTILIZATION OF IR AND LRMS ANALYSIS RESULTS FOR COMPOUND AND CATEGORY IDENTIFICATION

The previous sections of this report dealt with either IR or LRMS for compound and category identification, but the two techniques have not been discussed together. The goal of Level 1, however, is to make composite assignments based on both sets of information. In this study, in general, the IR and LRMS analysts worked separately to begin with and then came together to make the composite assignments. In cases where they worked together throughout the process, the analysts usually reported their results clearly enough so that differentiation could still be made as to whether a compound/category assignment was made based on IR, LRMS, or both. Because the LRMS data are typically given more weight in Level 1 assignments (categories found by LRMS tend to be the ones reported on the Level 1 organic summary tables), the impact of IR on LRMS will be discussed first followed by a discussion of cases where the IR interpretation was changed based on LRMS.

Table 52 shows the changes made in the LRMS interpretations by the LRMS analyst after seeing the IR interpretations. "A" made no changes in the test spectra and tar sample interpretation but did delete one compound, anthrone, from test mixture LC5 due to a poor IR match. Actually, anthrone was present in mixture LC5. Also, in mixture LC6, hydroxyanthraquinone was changed to 9-fluorenone-carboxylic acid and fluorene carboxylic acid. Tables 53 through 56 show that, following a review of both IR and LRMS results, no changes were made in the category/compound assignments for the test spectra and a net of one additional category/compound was correctly identified in the test mixtures.

"B" made several changes based on the IR results. In the test spectra, acridine and fluorenone were changed to carbazole and ethyl carbazole in LC5a, and pyridone was added to LC6a. Carboxyfluorenone was confirmed as 9-fluorenone-carboxylic acid in mixture LC6 and numerous categories of

TABLE 52. CHANGES MADE IN LRMS INTERPRETATIONS BY THE LRMS ANALYST
AFTER SEEING IR INTERPRETATIONS

Sample	"A"	"B"	"C"	"D"
(1) Test spectra LC4a	NC	NC	Anthracene major component Phenanthrene <u>minor</u> component Dibenzylanthracene <u>major</u> component	NC
LC4b	NC	NC	Anthracene, phenanthrene same amounts	NC
LC5a	NC	Acridone and fluorenone were changed to carbazole and ethyl carbazole	Carbazole <u>confirmed</u> Ethyl carbazole <u>confirmed</u>	NC
LC5b	NC	NC	Benzoquinoline favored over phenanthradine Phenazine <u>major</u> component Anthraquinone	Acridine, fluorenone added
LC6a	NC	Pyridone or pyridinol, pyrrole were listed; previously nothing	Pyridone <u>confirmed</u>	Anthraquinone, 2-Hydroxyanthraquinone added
LC6b	NC	NC	9-Fluorenone-4-carboxylic acid <u>major</u> component	NC
(2) Test mixtures LC5	(1) Changed fluorenone to benzocinnoline (2) Deleted anthrone due to poor IR match	NC	1,10-Phenanthroline <u>minor</u> Phenazine <u>major</u> Acridine <u>minor</u> 7,8-Benzoquinoline <u>minor</u> Anthraquinone <u>minor</u> 2,6-Dimethylquinoline <u>minor</u>	IR added but reason not given
LC6	Changed hydroxyanthraquinone to 9-fluorenone-4-carboxylic acid Added fluorenone carboxylic acid	Carboxyfluorenone changed to 9-fluorenone-4-carboxylic acid	9-Fluorenone, instead of just "fluorenone" 9-Fluorenone-4-COOH <u>major</u>	Added aromatic acids

(continued)

TABLE 52 (continued)

Sample	"A"	"B"	"C"	"D"
(3) Tar sample Tar LC4	NC	Carbazole listed instead of aliphatic hydrocarbons, carbonyl, nitrile	NC (IR suggested alcohols)	Ketones, fused ring hydrocarbons added
Tar LC5	NC	Carbonyl, sulfonate fused ring aromatic or heteroaromatic added	NC (IR very weak)	Esters added
Tar LC6	NC	Aromatic amines, aliphatic hydrocarbon	Phenol <u>major</u> component	Esters, acids, ketons added

NC = No change from previous analysis.

TABLE 53. SPECTRAL INTERPRETATION TEST CATEGORY ASSIGNMENTS
FOLLOWING REVIEW OF BOTH IR AND LRMS RESULTS

Category	"A"	"B"	"C"	"D"
LC4a				
Fused alternate, nonalter- nate hydrocarbons	Yes	Yes	Yes	Yes
LC4b				
Fused alternate, nonalter- nate hydrocarbons	Yes	Yes	Yes	Yes
LC5a				
Fused alternate, nonalter- nate hydrocarbons	No	No	Yes	No
Heterocyclic nitrogen com- pounds	Yes	Yes*	Yes	Yes
LC5b				
Heterocyclic nitrogen com- pounds	Yes	Yes*	Yes	Yes
Ketones	Yes	Yes*	Yes	Yes
LC6a				
Heterocyclic nitrogen com- pound or phenol or ketone	Yes	Yes*†	Yes	Yes†
Phenol	Yes	No	Yes	Yes†
LC6b				
Ketone	No	$\frac{1}{2}$	$\frac{1}{2}$	Yes
Phenol	Yes	No	No	No
Acid	No	Yes	Yes	No
Acid or ether	No	$\frac{1}{2}$	Yes	No
Ketone or acid	No	Yes	Yes	$\frac{1}{2}$
Total correct out of possible 13	8	9	11 $\frac{1}{2}$	8 $\frac{1}{2}$
Total correct by LRMS alone	8	8	11 $\frac{1}{2}$	6 $\frac{1}{2}$

Yes = Correct assignment.

No = Incorrect assignment.

*Made by RTI because contractor did not make assignment.

†IR changed LRMS.

TABLE 54. TEST MIXTURE CATEGORY ASSIGNMENTS FOLLOWING
REVIEW OF BOTH IR AND LRMS RESULTS

Category	"A"	"B"	"C"	"D"
LC5				
Fused alternate, nonalter- nate hydrocarbons	Yes	No	Yes	Yes
Heterocyclic nitrogen compounds	Yes	Yes	Yes	Yes
Ketones	Yes	Yes	Yes	Yes
LC6				
Ketones	Yes	Yes	Yes	Yes
Acids*	Yes†	Yes	Yes	Yes†
Phenols	No	No	Yes	Yes
Total correct out of 6	5	4	6	6
Total correct by LRMS alone	4	4	6	5

Yes = Correct assignment.

No = Incorrect assignment.

*9-Fluorenone-4-carboxylic acid was placed in acid category.

†IR changed LRMS.

TABLE 55. SPECTRAL INTERPRETATION TEST COMPOUND ASSIGNMENTS
FOLLOWING REVIEW OF BOTH IR AND LRMS RESULTS

Compound	"A"	"B"	"C"	"D"
LC4a				
Naphthalene	Yes	No	Yes	Yes
Anthracene	Yes	Yes	Yes	Yes
9-Methyl anthracene	Yes	Yes	Yes	Yes
Phenanthrene	Yes	Yes	Yes	Yes
9,10-Dimethyl anthracene	Yes	Yes	Yes	Yes
LC4b				
Naphthalene	Yes	No	Yes	Yes
Anthracene	Yes	Yes	Yes	Yes
9-Methyl anthracene	Yes	Yes	Yes	Yes
Phenanthrene	Yes	Yes	Yes	Yes
9,10-Dimethyl anthracene	Yes	Yes	Yes	Yes
2,3-Dimethyl naphthalene	Yes	No	Yes	Yes
LC5b				
7,8-Benzoquinoline	Yes	Yes	Yes	Yes†
Phenanthradine	Yes	Yes	Yes	Yes†
1,10-Phenanthroline	No	No	No	No
Phenazine	No	No	Yes	No
Anthrone	No	No	No	No
LC5a				
Fluorene	No	No	No	No
2,3-Benzofluorene	No	No	Yes	No
n-Ethyl carbazole	No	Yes*	Yes	Yes
2-Methyl indole	Yes	No	Yes	Yes
Carbazole	Yes	Yes*	Yes	Yes
2,3-Dimethyl indole	Yes	No	Yes	Yes
LC6a				
2-Hydroxy pyridine	Yes	Yes*	Yes	No
2,6-Dimethyl phenol	Yes	No	Yes	No
0-0'Biphenol	Yes	No	Yes	No
LC6b				
9-Fluorenone	No	No	No	No
2,6-Dimethyl phenol	No	No	No	No
0-Phenoxybenzoic acid	No	No	Yes	No
1-Fluorene carboxylic acid	No	Yes	Yes	No
9-Fluorenone-4-carboxylic acid	No	Yes†	Yes	No
Total correct out of 30	19	15	25	17
Total correct by LRMS alone	19	12	25	15-17

Yes = Correct assignment.

No = Incorrect assignment.

*IR changed LRMS.

†LRMS changed IR.

TABLE 56. TEST MIXTURE COMPOUND ASSIGNMENTS FOLLOWING
REVIEW OF BOTH IR AND LRMS RESULTS

Compound	"A"	"B"	"C"	"D"
LC5				
Fluorene	No	No	Yes	Yes
2,3-Benzofluorene	No	No	Yes	Yes
7,8-Benzoquinoline	Yes	Yes	Yes	No
1,10-Phenanthroline	No	No	Yes	No
Phenazine	No	No	Yes	No
2,6-Dimethylquinoline	No	Yes	Yes	Yes
Anthrone	No*	No	No	No
9-Fluorenone	Yes	Yes	Yes	Yes
1-Fluorene carboxylic acid	Yes*	No	Yes	No
9-Fluorenone-4-carboxylic acid	Yes*	Yes	Yes	No
2-Methyl-1-tetralone	No	No	Yes	No
2-t-Butyl phenol	No	No	Yes	Yes
2-Methyl-1,4-naphthoquinone	No	No	Yes	No
Total correct out of 13	4	4	12	5
Total correct by LRMS alone	3	4	12	5

No = Incorrect assignment.

Yes = Correct assignment.

*IR changed LRMS.

compounds were added to the tar sample results where previously only aliphatic hydrocarbons were listed. Because of these changes, a net of three additional compounds was added to "B's" overall spectral test results and one additional category was identified; no changes occurred in the test mixtures results.

"C" used the IR results to confirm and/or semiquantitate the components identified. No new categories or compounds were correctly identified so no net change in the number of correct assignments occurred.

"D's" IR results added acridine and fluorenone to test spectra LC5b although only the benzoquinoline isomer acridine was actually present. Also, it was not clear whether the IR analyst actually found acridine and fluorenone separately or helped confirm the LRMS identification of these two compounds. Anthraquinone and 2-hydroxy-anthraquinone were added to spectra LC6a where previously phenyl ether (OH) was the listing. The category aromatic acids was added to mixture LC6, and esters, ketones, and acids were added to the tar sample results. Although these changes did not markedly affect the test spectra compound assignments, two additional categories were listed. Also, one new category, acids, was correctly added to the test mixture results.

In general, then, the IR data helped to confirm categories/compounds indicated by the LRMS and to add additional categories such as acids when the LRMS results were inconclusive.

Only in a few cases was the IR interpretation changed by the LRMS and these changes were usually only cosmetic in nature (see Table 57).

TABLE 57. CHANGES MADE IN IR INTERPRETATIONS BY THE IR ANALYST
AFTER SEEING LRMS INTERPRETATIONS

Sample	"A"	"B"	"C"	"D"
Test spectra				
LC4a	NC	NC	NC	NC
LC4b	NC	NC	NC	NC
LC5a	NC	NC	NC	NC
LC5b	NC	Acridine added	NC	NC
LC6a	NC	NC	NC	NC
LC6b	NC	9-Fluorenone-2-carboxylic acid added	NC	NC
Test mixtures				
LC5	NC	NC	NC	Quinoline changed to dimethyl quinoline
LC6	NC	NC	NC	NC
Tar sample				
LC4	NC	NC	NC	NC
LC5	NC	NC	NC	NC
LC6	NC	NC	NC	Heterocyclic nitrogen compound added

SECTION 8

REFERENCES

- Bellamy, L. J., 1958, *The Infrared Spectra of Complex Molecules*, 2nd Edition, New York: Wiley and Sons.
- Butterworths and Verlag Chemie, *Documentation of Molecular Spectroscopy*, 38 Kingsway, London, W.C.2, England.
- Cleland, J. G., and G. L. Kingsbury, 1977, *Multimedia Environmental Goals for Environmental Assessment*, Volume II, MEG Charts and Background Information, EPA-600/7-77-1366.
- Colthup, N. B., 1950, *J. Opt. Soc. Am.*, 40:397.
- Colthup, N. B., L. H. Daly, and S. E. Wiberley, 1964, *Introduction to Infrared and Raman Spectroscopy*, New York: Academic Press.
- Dow Chemical Company, *IR Spectral Assignment Chart*, Midland, Michigan.
- Eight Peak Index of Mass Spectra, Imperial Chemical Industry, Ltd., 1970, First Edition, Mass Spectrometry Data Center, Alder Maston, Reading, United Kingdom.
- Heller, S. R., and G. W. A. Milne, 1978, *EPA/NIH Spectral Data Base*, U.S. Department of Commerce.
- Lentzen, D. E., D. E. Wagoner, E. D. Estes, and W. F. Gutknecht, 1978, *IERL-RTP Procedures Manual: Level 1 Environmental Assessment* (Second Edition), EPA-600/7-78-201.
- Lumpkin, H. E., and T. Aczel, 1977, *Identification of Aromatic Multi-sulfur Compound Types in Fossil Fuel Fractions*, presented at the Twenty-fifth Annual Conference on Mass Spectrometry and Allied Topics, Washington, D.C., May 29-June 3, 1977.
- Nakanishi, Koji, 1962, *Practical Infrared Absorption Spectroscopy*, San Francisco: Holden-Day, Inc.
- Rao, C. N. R., 1963, *Chemical Applications of Infrared Spectroscopy*, New York: Academic Press.
- Sadtler Research Laboratories, Inc., *Sadtler Standard Spectra*, 3316 Spring Garden Street, Philadelphia, Pennsylvania 19104.

APPENDIX A
VERIFICATION OF IR BANDS PRESENT IN TEST SPECTRA

TABLE A-1. VERIFICATION OF LC4a
Compound--Anthracene

Literature Spectrum			Test Mixture Spectrum		
cm ⁻¹	Intensity	Comment	cm ⁻¹	Intensity	Comment
3020	M	Sharp	3010	W	Shoulder
1930	W	Broad	1950-1900	W	Broad
1810	W	Sharp	1805	W	Sharp
1780	W	Sharp	1780	W	Sharp
1725	W	Sharp	1720	W	Broad
1620	M	Sharp	1620	S	Sharp
1530	W	Sharp	1535, 1525	M,W	Sharp, shoulder
1450	M	Sharp	1445	M	Sharp
1397	W	Sharp	1405, 1390	W,M	Sharp, sharp
1315	M	Sharp	1320	M	Sharp
1270	M	Sharp	1280, 1275	W,M	Sharp
1167	W	Sharp	1170, 1160	M	Doublet
1150	M	Sharp	1150	S	Sharp
1000	M	Sharp	1000	S	Sharp
960	S	Sharp	960	S	Sharp
912	W	Sharp	910	M	Sharp
890	S	Sharp	885	S	Sharp
740	M	Sharp	755, 745	S	Doublet part of a large peak
725	S	Sharp	730, 725	S,M	Sharp, shoulder
600	M	Sharp	600	M	Sharp
480	M	Sharp	475	S	Sharp
380	W	Sharp	--	--	--

TABLE A-2. VERIFICATION OF LC4a
Compound--Phenanthrene

Literature Spectrum			Test Mixture Spectrum		
cm ⁻¹	Intensity	Comment	cm ⁻¹	Intensity	Comment
3050	M	Sharp	3050	S	Sharp
3020	M	Shoulder	3010	W	Shoulder
1952	W	Broad	1950-1900	W	Broad
1918	W	Broad	1950-1900	W	Broad
1895	W	Broad	1950-1900	W	Broad
1850	W	Broad	--	--	--
1820	W	Broad	--	--	--
1760	W	Broad	--	--	--
1620	W	Sharp	1620	S	Sharp
1600	W	Sharp	--	--	--
1500	M	Sharp	--	--	--
1458	M	Sharp	--	--	--
1440	M	Shoulder	1445	M	Sharp
1430	M	Sharp	--	--	--
1300	M	Sharp	--	--	--
1250	M	Sharp	1240	W	--
1140	M	Sharp	1150	S	Sharp
1093	W	Sharp	--	--	--
1040	W	Sharp	1040	W	Shoulder
1000	W	Sharp	1000	S	Sharp
950	M	Sharp	960	S	Sharp
890	W	Sharp	885	S	Sharp
875	M	Sharp	--	--	--
820	S	Sharp	825, 815	W,M	Shoulder, sharp
745	S	Sharp	755, 745	S	Doublet part of a large peak
720	M	Sharp	730, 725	S,M	Sharp, shoulder
620	W	Sharp	--	--	--
500	W	Sharp	--	--	--
435	M	Sharp	--	--	--
370	M	Sharp	--	--	--

TABLE A-3. VERIFICATION OF LC4a
Compound--9,10-Dimethylantracene

Literature Spectrum			Test Mixture Spectrum		
cm ⁻¹	Intensity	Comment	cm ⁻¹	Intensity	Comment
3440	M	Sharp	3430	M	Broad, water peak
2920	W	Broad	2930	W	Broad
2490	W	Sharp	--	--	--
1930	W	Sharp	1950-1900	W	Broad
1910	W	Sharp	1950-1900	W	Broad
1895	W	Sharp	1950-1900	W	Broad
1810	W	Sharp	1805	W	Sharp
1790	W	Sharp	--	--	--
1700	W	Sharp	1690-1720	W	Broad
1620	M	Sharp	1620	S	Sharp
1527	W	Sharp	1535	M	Sharp
1445	M	Sharp	1445	M	Sharp
1387	M	Sharp	1390	M	Sharp
1365	M	Sharp	1365	M	Sharp
1278	W	Sharp	1280	W	--
1190	W	Sharp	1180	W	--
1165	W	Sharp	1160, 1170	M	Doublet
1030	M	Sharp	1040	W	Shoulder
990	W	Sharp	1000, 980	S,W	Sharp, shoulder
950	W	Sharp	960	S	Sharp
850	W	Sharp	850	W	Shoulder
818	W	Sharp	815	M	Sharp
750	S	Sharp	755, 745	S	Doublet part of a large peak
605	M	Sharp	600	M	Sharp
590	M	Sharp	580	M	Sharp
400	M	Sharp	395	M	Sharp

TABLE A-4. VERIFICATION OF LC4a
Compound--Naphthalene

Literature Spectrum			Test Mixture Spectrum		
cm ⁻¹	Intensity	Comment	cm ⁻¹	Intensity	Comment
3040	S	Sharp	3050	S	Sharp
3020	M	Sharp	3010	W	Shoulder
3000	W	Sharp	3010	W	Shoulder
2840	W	Sharp	--	--	--
2405	W	Sharp	--	--	--
2270	W	Sharp	--	--	--
1950	M	Sharp	1950-1900	W	Broad
1940	W	Sharp	1950-1900	W	Broad
1920	M	Sharp	1950-1900	W	Broad
1850	M	Sharp	--	--	--
1820	W	Sharp	--	--	--
1780	M	Sharp	1780	W	Sharp
1740	W	Sharp	--	--	--
1680	M	Sharp	1690-1720	W	Broad
1600	M	Sharp	--	--	--
1580	M	Sharp	--	--	--
1510	W	Sharp	--	--	--
1500	M	Sharp	--	--	--
1420	W	Sharp	--	--	--
1390	S	Sharp	1390	M	Sharp
1360	S	Sharp	1360	M	Sharp
1300	W	Sharp	--	--	--
1268	S	Sharp	1275	M	Sharp
1240	M	Sharp	1240	W	--
1200	M	Sharp	--	--	--
1140	M	Sharp	1150	S	Sharp
1125	M	Sharp	--	--	--
1000	M	Sharp	1000	S	Sharp
980	M	Sharp	980	W	Shoulder
960	S	Sharp	960	S	Sharp

(continued)

TABLE A-4 (continued)

Literature Spectrum			Test Mixture Spectrum		
cm ⁻¹	Intensity	Comment	cm ⁻¹	Intensity	Comment
840	M	Sharp	835	M	Sharp
815	M	Sharp	815	M	Sharp
783	S	Sharp	775	S	Sharp
743	M	Sharp	745, 755	S	Doublet part of a large peak
725	M	Sharp	725	M	Shoulder
620	M	Sharp	--	--	--
430	M	Sharp	--	--	--
352	W	Sharp	--	--	--

TABLE A-5. VERIFICATION OF LC4a
Compound--9-Methylanthracene

Literature Spectrum			Test Mixture Spectrum		
cm ⁻¹	Intensity	Comment	cm ⁻¹	Intensity	Comment
3080	M	Sharp	--	--	--
3050	S	Sharp	3050	S	Sharp
3020	M	Sharp	3010	W	Shoulder
2925	M	Sharp	2930	W	Broad
2865	W	Sharp	--	--	--
2500	W	Sharp	--	--	--
1940	W	Sharp	1950-1900	W	Broad
1910	W	Sharp	1950-1900	W	Broad
1890	W	Sharp	1950-1900	W	Broad
1835	W	Sharp	--	--	--
1800	W	Broad	1805	W	Sharp
1770	W	Sharp	1780	W	Sharp
1720	W	Sharp	1720-1690	W	Broad
1675	M	Shoulder	--	--	--
1665	M	Sharp	--	--	--
1620	S	Sharp	1620	S	Sharp
1600	M	Sharp	--	--	--
1560	W	Sharp	--	--	--
1525	W	Sharp	1525	W	Shoulder
1483	W	Sharp	--	--	--
1460	W	Sharp	--	--	--
1442	M	Sharp	1445	M	Sharp
1410	M	Sharp	1405	W	Sharp
1390	M	Sharp	1390	M	Sharp
1370	M	Sharp	1365	M	Sharp
1350	S	Sharp	1350	M	Sharp
1310	M	Broad	1320	M	Sharp
1280	M	Sharp	1280	W	--
1250	W	Sharp	1240	W	--
1180	M	Sharp	1180	W	--

TABLE A-5 (continued)

Literature Spectrum			Test Mixture Spectrum		
cm ⁻¹	Intensity	Comment	cm ⁻¹	Intensity	Comment
1158	M	Sharp	1170, 1160, 1150	M,S	Doublet, sharp
1091	W	Sharp	--	--	--
1039	W	Sharp	1040	W	Shoulder
995	W	Sharp	1000	S	Sharp
970	W	Sharp	980, 960	W,S	Shoulder, sharp
942	W	Sharp	--	--	--
882	M	Sharp	885	S	Sharp
860	M	Sharp	860	W	Shoulder
840	M	Sharp	835	M	Sharp
780	M	Sharp	775	S	Sharp
728	S	Sharp	730, 725	S,M	Sharp, shoulder
695	S	Sharp	--	--	--
660	W	Sharp	--	--	--
640	W	Sharp	--	--	--
630	W	Sharp	--	--	--
620	W	Sharp	--	--	--
600	M	Sharp	600	M	Sharp
582	W	Sharp	580	M	Sharp
570	W	Sharp	580	M	Sharp
530	M	Sharp	530	M	Sharp
480	W	Sharp	475	S	Sharp
450	W	Sharp	--	--	--
400	M	Sharp	395	M	Sharp
360	W	Sharp	--	--	--
325	W	Sharp	--	--	--

TABLE A-6. VERIFICATION OF LC4b
Compound--9,10-Dimethylantracene

Literature Spectrum			Test Mixture Spectrum		
cm ⁻¹	Intensity	Comment	cm ⁻¹	Intensity	Comment
3440	M	Sharp	3500-3400	W	Broad, H ₂ O
2920	W	Broad	2930	W	Broad
2490	W	Sharp	--	--	--
1930	W	Sharp	1950-1900	W	Broad
1910	W	Sharp	1950-1900	W	Broad
1895	W	Sharp	1950-1900	W	Broad
1810	W	Sharp	1805	W	Very weak
1790	W	Sharp	--	--	--
1700	W	Sharp	--	--	--
1620	M	Sharp	1620	M	Sharp
1527	W	Sharp	1535	M	Sharp
1445	M	Sharp	1450	M	Broad
1387	M	Sharp	1385	W	Broad
1365	M	Sharp	1365	W	--
1278	W	Sharp	1280, 1270	W,W	Shoulder, sharp
1190	W	Sharp	--	--	--
1165	W	Sharp	1170	W	Sharp
1030	M	Sharp	--	--	--
990	W	Sharp	1000	M	Sharp
950	W	Sharp	960, 950	M	Sharp, doublet
850	W	Sharp	--	--	--
818	W	Sharp	820	S	Sharp
750	S	Sharp	--	--	--
605	M	Sharp	600	W	Sharp
590	M	Sharp	580	W	--
400	M	Sharp	--	--	--

TABLE A-7. VERIFICATION OF LC4b
Compound--Anthracene

Literature Spectrum			Test Mixture Spectrum		
cm ⁻¹	Intensity	Comment	cm ⁻¹	Intensity	Comment
3020	M	Sharp	3020	W	Shoulder
1930	W	Broad	1950-1900	W	Broad
1810	W	Sharp	1805	W	Very weak
1780	W	Sharp	--	--	--
1725	W	Sharp	--	--	--
1620	M	Sharp	1620	M	Sharp
1530	W	Sharp	1535	M	Sharp
1450	M	Sharp	1450	M	Broad
1397	W	Sharp	--	--	--
1315	M	Sharp	--	--	--
1270	M	Sharp	1270	W	Sharp
1167	W	Sharp	1170	W	Sharp
1150	M	Sharp	1150, 1140	M	Doublet
1000	M	Sharp	1000	M	Sharp
960	S	Sharp	960, 950	M	Doublet, sharp
912	W	Sharp	910	W	Shoulder
890	S	Sharp	885	S	Sharp with 2 shoulders at 880 & 870
740	M	Sharp	735	S	Broad with shoulders at 790, 780, 755, 715
725	S	Sharp	735	S	Broad with shoulders at 790, 780, 755, 715
600	M	Sharp	600	W	Sharp
480	M	Sharp	490, 475	M,S	Sharp, sharp
380	W	Sharp	--	--	--

TABLE A-8. VERIFICATION OF LC4b
Compound--Phenanthrene

Literature Spectrum			Test Mixture Spectrum		
cm ⁻¹	Intensity	Comment	cm ⁻¹	Intensity	Comment
3050	M	Sharp	3050	M	Sharp
3020	M	Shoulder	3020	W	Shoulder
1952	W	Broad	1950-1900	W	Broad
1918	W	Broad	1950-1900	W	Broad
1895	W	Broad	1950-1900	W	Broad
1850	W	Broad	--	--	--
1820	W	Broad	--	--	--
1760	W	Broad	--	--	--
1620	W	Sharp	1620	M	Sharp
1600	W	Sharp	1590	W	Sharp
1500	M	Sharp	1500	M	Sharp
1458	M	Sharp	1450	M	Broad
1440	M	Shoulder	1450, 1430	M,M	Broad, sharp
1430	M	Sharp	1430	M	Sharp
1300	M	Sharp	--	--	--
1250	M	Sharp	1245	M	Sharp
1140	M	Sharp	1150-1140	M	Doublet
1093	W	Sharp	1090	W	Broad
1040	W	Sharp	1035, 1025	W	Doublet, sharp
1000	W	Sharp	1000	M	Sharp
950	M	Sharp	960, 950	M	Doublet, sharp
890	W	Sharp	885	S	Sharp with 2 shoulders at 880 and 890
875	M	Sharp	885	S	Sharp with 2 shoulders at 880 and 870
820	S	Sharp	820	S	Sharp
745	S	Sharp	735	S	Broad with shoulders at 790, 780, 755, 715
720	M	Sharp	--	--	--
620	W	Sharp	620	W	--
500	W	Sharp	490	M	Sharp
435	M	Sharp	430	M	Sharp
370	M	Sharp	--	--	--

TABLE A-9. VERIFICATION OF LC4b
Compound--Naphthalene

Literature Spectrum			Test Mixture Spectrum		
cm ⁻¹	Intensity	Comment	cm ⁻¹	Intensity	Comment
3040	S	Sharp	3050	M	Sharp
3020	M	Sharp	3020	W	Shoulder
3000	W	Sharp	--	--	--
2840	W	Sharp	--	--	--
2405	W	Sharp	--	--	--
2270	W	Sharp	--	--	--
1950	M	Sharp	1950-1900	W	Broad
1940	W	Sharp	1950-1900	W	Broad
1920	M	Sharp	1950-1900	W	Broad
1850	M	Sharp	--	--	--
1820	W	Sharp	--	--	--
1780	M	Sharp	--	--	--
1740	W	Sharp	--	--	--
1680	M	Sharp	--	--	--
1600	M	Sharp	--	--	--
1580	M	Sharp	590	W	Sharp
1510	M	Sharp	1500	M	Sharp
1500	W	Sharp	1500	M	Sharp
1420	W	Sharp	1430, 1420*	M,W	Sharp, shoulder
1390	S	Sharp	1385	W	Broad
1360	S	Sharp	1365	W	--
1300	W	Sharp	--	--	--
1268	S	Sharp	1270	W	Sharp
1200	M	Sharp	--	--	--
1140	M	Sharp	1150-1140	M	Doublet
1125	M	Sharp	--	--	--
1000	M	Sharp	1000	M	Sharp
980	M	Sharp	--	--	--
960	S	Sharp	960, 950	M	Doublet, sharp
840	M	Sharp	--	--	--
815	M	Sharp	820	S	Sharp

TABLE A-9. (continued)

Literature Spectrum			Test Mixture Spectrum		
cm ⁻¹	Intensity	Comment	cm ⁻¹	Intensity	Comment
783	S	Sharp	--	--	--
743	M	Sharp	735	S	Broad with shoulders at 790, 780, 755, 715
725	M	Sharp	735	S	Broad with shoulders at 790, 780, 755, 715
620	M	Sharp	620	W	--
430	M	Sharp	430	M	Sharp
352	W	Sharp	--	--	--

*Mixture peak is not found in library spectra of mixture compounds.

TABLE A-10. VERIFICATION OF LC4b
Compound--9-Methylantracene

Literature Spectrum			Test Mixture Spectrum		
cm ⁻¹	Intensity	Comment	cm ⁻¹	Intensity	Comment
3080	M	Sharp	--	--	--
3050	S	Sharp	3050	M	Sharp
3020	M	Sharp	3020	W	Shoulder
2925	M	Sharp	2930	W	Broad
2865	W	Sharp	--	--	--
2500	W	Sharp	--	--	--
1940	W	Sharp	1950-1900	W	Broad
1910	W	Sharp	1950-1900	W	Broad
1890	W	Sharp	1950-1900	W	Broad
1835	W	Sharp	1835	W	Very weak
1800	W	Broad	1805	W	Very weak
1770	W	Sharp	--	--	--
1720	W	Sharp	--	--	--
1675	M	Shoulder	--	--	--
1665	M	Sharp	--	--	--
1620	S	Sharp	1620	M	Sharp
1600	M	Sharp	1590	W	Sharp
1560	W	Sharp	--	--	--
1525	W	Sharp	1535	M	Sharp
1483	W	Sharp	--	--	--
1460	W	Sharp	1450	M	Broad
1442	M	Sharp	1450	M	Broad
1410	M	Sharp	1420*	W	Shoulder
1390	M	Sharp	1385	W	Broad
1370	M	Sharp	1365	W	--
1350	S	Sharp	1350	W	--
1310	M	Broad	--	--	--
1280	M	Sharp	1280	W	Shoulder
1250	W	Sharp	1250	M	Sharp
1180	M	Sharp	1170	W	Sharp

(continued)

TABLE A-10 (continued)

Literature Spectrum			Test Mixture Spectrum		
cm ⁻¹	Intensity	Comment	cm ⁻¹	Intensity	Comment
1158	M	Sharp	1150, 1140	M	Doublet
1091	W	Sharp	1090	W	Broad
1039	W	Sharp	1035, 1025	W	Doublet, sharp
995	W	Sharp	1000	M	Sharp
970	W	Sharp	960, 950	M	Doublet, sharp
942	W	Sharp	960, 950	M	Doublet, sharp
882	M	Sharp	885	S	Sharp with 2 shoulders at 880 and 870
860	M	Sharp	--	--	--
840	M	Sharp	--	--	--
780	M	Sharp	--	--	--
728	S	Sharp	735	S	Broad with shoulders at 790, 780, 755, 715
695	S	Sharp	--	--	--
660	W	Sharp	--	--	--
640	W	Sharp	--	--	--
630	W	Sharp	625, 620	W	--
620	W	Sharp	625, 620	W	--
600	M	Sharp	600	W	Sharp
582	W	Sharp	580	W	--
570	W	Sharp	580	W	--
530	M	Sharp	530	W	--
480	W	Sharp	490, 475	M,S	Sharp, sharp
450	W	Sharp	440	W	Sharp
400	M	Sharp	--	--	--
360	W	Sharp	--	--	--
325	W	Sharp	--	--	--

*Mixture peak is not found in library spectra of mixture components.

TABLE A-11. VERIFICATION OF LC4b
Compound--2,3-Dimethylnaphthalene

Literature Spectrum			Test Mixture Spectrum		
cm ⁻¹	Intensity	Comment	cm ⁻¹	Intensity	Comment
3440	M	Broad	3500-3400	W	Broad, H ₂ O
3120	W	Sharp	--	--	--
3040	M	Sharp	3050	M	Sharp
3000	W	Sharp	--	--	--
2970	W	Sharp	--	--	--
2920	M	Sharp	2930	W	Broad
1776	W	Sharp	--	--	--
1700	W	Broad	--	--	--
1640	W	Broad	--	--	--
1600	M	Broad	1590	W	Sharp
1500	M	Sharp	1500	M	Sharp
1450	M	Sharp	1450	M	Broad
1430	M	Sharp	1430	M	Sharp
1380	M	Sharp	1385	W	Broad
1330	W	Sharp	--	--	--
1275	W	Sharp	1280, 1270	W,W	Shoulder, sharp
1230	W	Sharp	--	--	--
1150	W	Sharp	1150-1140	M	Doublet
1090	W	Broad	1090	W	Broad
1020	M	Sharp	1035-1025	W	Doublet, sharp
950	M	Sharp	960, 950	M	Doublet, sharp
870	S	Sharp	--	--	--
740	S	Sharp	735	S	Broad with shoulders at 790, 780, 755, 715
480	M	Sharp	490, 475	M,S	Sharp, sharp
410	W	Sharp	--	--	--
360	M	Sharp	--	--	--

TABLE A-12. VERIFICATION OF LC5a
Compound--2,3-Dimethylindole

Literature Spectrum			Test Mixture Spectrum		
cm ⁻¹	Intensity	Comment	cm ⁻¹	Intensity	Comment
3390	S	Sharp	--	--	--
3030	W	Sharp	--	--	--
2915	S	Sharp	--	--	--
2841	M	Shoulder	--	--	--
1852	W	Sharp	--	--	--
1739	W	Sharp	--	--	--
1605	W	Sharp	1600	S	Sharp
1449	S	Sharp	1455	S	Sharp
1370	M	Sharp	--	--	--
1325	M	Sharp	1330	S	Sharp
1294	S	Sharp	1285	W	Sharp
1234	M	Sharp	1235	S	Sharp
1212	W	Shoulder	1210	W	Shoulder
1093	W	Sharp	1090	M	Sharp
1000	M	Sharp	1000	M	Sharp
957	W	Broad	960	W	Sharp
913	W	Sharp	--	--	--
735	S	Broad	750, 725	S	Sharp, doublet
635	M	Broad	620, 630	W,M	Doublet, sharp

TABLE A-13. VERIFICATION OF LC5a
Compound--2-Methylindole

Literature Spectrum			Test Mixture Spectrum		
cm ⁻¹	Intensity	Comment	cm ⁻¹	Intensity	Comment
3413	S	Sharp	3420	S	Sharp
2967	M	Sharp	2970	S	Sharp
2924	M	Sharp	2920	W	Sharp
2755	W	Sharp	--	--	--
2618	W	Sharp	--	--	--
2469	W	Sharp	--	--	--
1880	W	Sharp	1885	W	Broad
1751	W	Sharp	--	--	--
1667	W	Sharp	--	--	--
1613	W	Sharp	--	--	--
1587	M	Sharp	--	--	--
1550	M	Sharp	--	--	--
1456	S	Sharp	--	--	--
1408	S	Sharp	1400	W	Broad
1342	S	Sharp	1345	S	Sharp
1285	S	Sharp	1285	W	Sharp
1235	W	Sharp	1235	S	Sharp
1215	M	Sharp	1210	W	Shoulder
1153	W	Sharp	1155	S	Sharp
1136	W	Sharp	1130	M	Sharp
1029	M	Sharp	1020, 1010	W	Doublet
1013	M	Sharp	--	--	--
966	W	Broad	960	W	Sharp
921	W	Broad	930	M	Sharp
881	W	Broad	875	W	--
844	W	Broad	845	W	Sharp
778	S	Broad	785, 775	M	Doublet
746	S	Broad	750, 725	S	Strong doublet
656	W	Sharp	660	W	Sharp

TABLE A-14. VERIFICATION OF LC5a
Compound--Carbazole

Literature Spectrum			Test Mixture Spectrum		
cm ⁻¹	Intensity	Comment	cm ⁻¹	Intensity	Comment
3420	S	Sharp	3420	S	Sharp
3040	W	Sharp	3050	S	Sharp
1930	W	Sharp	1930	W	Broad
1890	W	Sharp	1885	W	Broad
1780	W	Sharp	1770	W	Broad
1620	W	Shoulder	--	--	--
1600	W	Sharp	1600	S	Sharp
1445	W	Sharp	--	--	--
1450	S	Sharp	1455	W	Sharp
1400	W	Sharp	1400	W	Broad
1330	W	Sharp	1330	S	Sharp
1240	W	Sharp	1235	S	Sharp
1205	W	Sharp	1210	W	Shoulder
1140	W	Sharp	1130	M	Sharp
990	W	Sharp	1000	M	Sharp
930	W	Sharp	930	M	Sharp
860,840	W	Doublet, sharp	860	W	--
760	W	Shoulder	750, 725	S	Sharp, doublet
740	M	Sharp	--	--	--
720	S	Sharp	--	--	--
570	W	Sharp	575	M,W	Doublet, sharp
450	W	Sharp	--	--	--

TABLE A-15. VERIFICATION OF LC5a
Compound--N-Ethylcarbazole (9-Ethylcarbazole)

Literature Spectrum			Test Mixture Spectrum		
cm ⁻¹	Intensity	Comment	cm ⁻¹	Intensity	Comment
3420	W	Broad	3420	S	Sharp
3050	W	Sharp	3050	S	Sharp
2970	M	Sharp	2970	S	Sharp
2940	W	Sharp	2930	W	Sharp
2880	W	Broad	--	--	--
1660	W	Sharp	--	--	--
1620	W	Sharp	--	--	--
1590	M	Sharp	--	--	--
1475	S	Sharp	1470	S	Sharp
1465	S	Sharp	--	--	--
1450	S	Sharp	1455	S	Sharp
1375	M	Sharp	1385	M	Sharp
1340	M	Shoulder	1345	S	Shoulder
1325	S	Sharp	1330	S	Sharp
1225	S	Sharp	1235	S	Sharp
1150	M	Sharp	1155	S	Sharp
1135	W	Doublet, sharp	1130	M	Sharp
1125	W	Doublet, sharp	1122	M	Sharp
1080	W	Sharp	1090	M	Sharp
1055	W	Sharp	1060	W	Sharp
1015	W	Broad	--	--	--
1000	W	Sharp	1000	M	Sharp
935, 945	W	Doublet, broad	930	M	Sharp
875	W	Sharp	875	W	--
840	W	Broad	845	W	Sharp
780	W	Sharp	785, 775	M	Doublet
750	S	Sharp	750, 725	M	Doublet
725	S	Sharp	--	--	--

(continued)

TABLE A-15. (continued)

Literature Spectrum			Test Mixture Spectrum		
cm ⁻¹	Intensity	Comment	cm ⁻¹	Intensity	Comment
610	W	Sharp	620, 630	W,M	Doublet, sharp
570	W	Sharp	575, 560	M,W	Doublet, sharp
550	W	Sharp	--	--	--
520	W	Sharp	510	W	Sharp
415	W	Sharp	425, 435	S	Doublet, sharp

TABLE A-16. VERIFICATION OF LC5a
Compound--Fluorene

Literature Spectrum			Test Mixture Spectrum		
cm ⁻¹	Intensity	Comment	cm ⁻¹	Intensity	Comment
3060	W	Shoulder	3050	S	Sharp
3030	W	Sharp	--	--	--
2900	W	Sharp	2890	W	--
1950	W	Sharp	--	--	--
1800	W	Broad	--	--	--
1470	W	Sharp	1470	S	Sharp
1450	W	Sharp	1455	S	Sharp
1400	W	Sharp	1400	W	Broad
1290, 1310	W	Doublet, sharp	1300	W	Sharp
1185	W	Sharp	1185	W	Sharp
1090, 1110	W	Doublet, sharp	1090	M	Sharp
1020	W	Sharp	1020, 1010	W	Doublet
1000	W	Sharp	1000	M	Sharp
950	W	Sharp	960	W	Sharp
860	W	Sharp	860	W	--
730	S	Sharp	750, 725	S	Strong sharp doublet
690	W	Sharp	--	--	--
625	W	Sharp	620, 630	W,M	Doublet, sharp
410	W	Sharp	--	--	--
360	W	Sharp	--	--	--

TABLE A-17. VERIFICATION OF LC5a
Compound--2,3-Benzofluorene

Literature Spectrum			Test Mixture Spectrum		
cm ⁻¹	Intensity	Comment	cm ⁻¹	Intensity	Comment
2932	S	Sharp	2930	W	Sharp
2857	M	Shoulder	--	--	--
1605	W	Broad	1600	S	Sharp
1464	M	Sharp	1470	S	Sharp
1404	M	Sharp	1400	W	Broad
1351	W	Sharp	1345	S	Sharp
1335	W	Sharp	1330	S	Sharp
1311	W	Sharp	1300	W	Sharp
1263	W	Sharp	--	--	--
1012	W	Sharp	1020, 1010	W	Doublet
952	M	Sharp	960	W	Sharp
881	W	Sharp	890	W	--
870	S	Sharp	875	W	--
814	W	Sharp	--	--	--
769	S	Sharp	785, 775	M	Doublet
758	S	Sharp	750, 725	S	Strong sharp doublet
723	S	Sharp	--	--	--

TABLE A-18. VERIFICATION OF LC5b
Compound--Phenazine

Literature Spectrum			Test Mixture Spectrum		
cm ⁻¹	Intensity	Comment	cm ⁻¹	Intensity	Comment
3280	W	Broad	3300-3600	M	Broad
3060	W	Sharp	3050	W	Broad
3030	W	Shoulder	--	--	--
3000	W	Sharp	--	--	--
1920	W	Broad	--	--	--
1650	W	Broad	1675	M	Sharp but broadens to include 2 shoulders at 1660 & 1650
1610	W	Broad	1620	W	Sharp
1555	W	Broad	--	--	--
1510	S	Sharp	1515	S	Sharp
1468	M	Sharp	1470	W	Sharp
1425	M	Sharp	1420	W	Sharp
1400	W	Sharp	1405	W	Sharp
1360	M	Shoulder	1360	M	Sharp
1350	M	Sharp	--	--	--
1320	W	Sharp	1300-1330	W	Broad
1255	W	Sharp	--	--	--
1205	W	Sharp	1210	W	--
1145	M	Sharp	1145	M	Sharp
1110	M	Broad	1110	W	Sharp
990	W	Sharp	995	W	--
955	W	Sharp	960	W	--
900	W	Sharp	905	W	Sharp
855	W	Sharp	860	W	Sharp
820	M	Sharp	820	S	Sharp
745	S	Sharp	750	S	Broad w/ shoulders at 775, 735, & 725
655	W	Sharp	660	W	Sharp
645	W	Sharp	--	--	--
630	W	Sharp	620	W	Sharp

(continued)

TABLE A-18 (continued)

Literature Spectrum			Test Mixture Spectrum		
cm^{-1}	Intensity	Comment	cm^{-1}	Intensity	Comment
610	W	Sharp	--	--	--
590	M	Sharp	595	M	Sharp
390	W	Sharp	395	W	Sharp

TABLE A-19. VERIFICATION OF LC5b
Compound--Phenanthradine

Literature Spectrum			Test Mixture Spectrum		
cm ⁻¹	Intensity	Comment	cm ⁻¹	Intensity	Comment
3065	W	Sharp	--	--	--
1620	M	Sharp	1620	W	Sharp
1590	S	Sharp	1585	W	Sharp
1570	S	Sharp	1575	W	Sharp
1530	M	Sharp	1525	W	Sharp
1490	M	Sharp	1490	W	Shoulder
1460	M	sharp	1460	W	Sharp
1440	M	Sharp	1445	W	Sharp
1400	M	Sharp	1405	W	Sharp
1390	M	Shoulder	--	--	--
1340	W	Sharp	--	--	--
1290	W	Sharp	1285	M	Sharp
1250	S	Sharp	--	--	--
1240	W	Shoulder	1240	W	Sharp
1200	M	Sharp	1210	W	--
1140	M	Sharp	1145	M	Sharp
1040	W	Sharp	1035	W	--
970	M	Sharp	960	W	--
800	W	Sharp	--	--	--
770	S	Sharp	750	S	Broad w/ shoulders at 775, 735, 725 and a medium shoulder at 700
760	S	Sharp	--	--	Shoulders at 775, 735, 725 & a medium shoulder at 700
720	S	Sharp	--	--	--
710	M	Shoulder	--	--	--
620	M	Sharp	620	W	Sharp
610	W	Shoulder	--	--	--
500	W	Sharp	495	W	Sharp

(continued)

TABLE A-19 (continued)

Literature Spectrum			Test Mixture Spectrum		
cm^{-1}	Intensity	Comment	cm^{-1}	Intensity	Comment
450	W	Sharp	450	W	Sharp
430	W	Sharp	430	W	Sharp
410	W	Sharp	410	W	Sharp

TABLE A-20. VERIFICATION OF LC5b
Compound--1,10-Phenanthroline

Literature Spectrum			Test Mixture Spectrum		
cm ⁻¹	Intensity	Comment	cm ⁻¹	Intensity	Comment
3030	M	Sharp	--	--	--
1950	W	Broad	--	--	--
1640	M	Sharp	--	--	--
1600	M	Sharp	--	--	--
1565	M	Sharp	1575	W	Sharp
1510	M	Sharp	1515	S	Sharp
1455	M	Shoulder	1460	W	Sharp
1430	S	Sharp	1430	W	Sharp
1360	M	Sharp	1360	M	Sharp
1325	W	Sharp	1300-1330	W	Broad
1300	W	Sharp	--	--	--
1275	W	Broad	1285	M	Sharp
1225	M	Sharp	--	--	--
1190	W	Sharp	1190	W	--
1160	M	Sharp	1170	W	Sharp
1110	M	Sharp	1110	W	Sharp
1095	M	Shoulder	1090	W	--
1050	W	Sharp	--	--	--
1000	W	Sharp	995	W	--
980	W	Sharp	--	--	--
955	W	Sharp	960	W	--
895	W	Broad	890	W	Sharp
865	S	Sharp	860	W	Sharp
848	S	Broad	848	M	Sharp
770	S	Sharp	--	--	Broad w/ shoulders at 775, 735, 725 & a medium shoulder at 700
740	S	Broad	750	S	--
720	M	Sharp	--	--	--

TABLE A-21. VERIFICATION OF LC5b
Compound--Anthrone

Literature Spectrum			Test Mixture Spectrum		
cm ⁻¹	Intensity	Comment	cm ⁻¹	Intensity	Comment
3060	M	Sharp	3050	W	Broad
3025	M	Sharp	--	--	--
2880	M	Sharp	--	--	--
2780	W	Sharp	--	--	--
2630	W	Broad	--	--	--
2480	W	Sharp	--	--	--
1840	W	Broad	--	--	--
1740	W	Broad	--	--	--
1660	S	Broad	--	--	--
1600	S	Broad	--	--	--
1540	W	Shoulder	--	--	--
1480	M	Sharp	1490	W	Shoulder
1468	S	Sharp	1470	W	Sharp
1452	S	Sharp	1445	W	Sharp
1400	S	Sharp	1405	W	Sharp
1390	W	Sharp	--	--	--
1350	M	Sharp	1360	M	Sharp
1310	S	Broad	1300-1330	W	Broad
1295	S	Shoulder	1285	M	Sharp
1260	M	Shoulder	--	--	--
1230	W	Sharp	1240	W	Sharp
1202	W	Sharp	1210	W	--
1177	S	Sharp	1170	W	Sharp
1158	S	Sharp	--	--	--
1115	W	Sharp	1110	W	Sharp
1090	M	Sharp	1090	W	--
1040	W	Sharp	1035	W	--
960	M	Sharp	960	W	--
940	S	Sharp	935	W	--

(continued)

TABLE A-21 (continued)

Literature Spectrum			Test Mixture Spectrum		
cm ⁻¹	Intensity	Comment	cm ⁻¹	Intensity	Comment
870	W	Sharp	--	--	--
860	W	Sharp	860	W	Sharp
840	W	Sharp	840	M	Sharp
815	M	Sharp	820	S	Sharp
790	W	Sharp	--	--	--
725	S	Shoulder	750	S	Broad w/shoulders at 775, 735, 725 & a medium shoulder at 700
718	S	Sharp	--	--	--
697	M	Shoulder	--	--	--
670	M	Sharp	660	W	Sharp
632	S	Sharp	--	--	--
580	W	Sharp	--	--	--
532	W	Sharp	--	--	--
460	M	Sharp	450	W	Sharp
400	W	Sharp	410	W	Sharp
360	W	Sharp	--	--	--
328	W	Sharp	--	--	--

TABLE A-22. VERIFICATION OF LC5b
Compound--7,8-Benzoquinoline

Literature Spectrum			Test Mixture Spectrum		
cm ⁻¹	Intensity	Comment	cm ⁻¹	Intensity	Comment
3030	M	Sharp	--	--	--
1613	M	Shoulder	1620	W	Sharp
1587	S	Sharp	1585	W	Sharp
1562	M	Shoulder	--	--	--
1515	M	Sharp	1515	S	Sharp
1428	S	Sharp	1430	W	Sharp
1399	S	Sharp	1405	W	Sharp
1316	M	Sharp	1300-1330	W	Broad
1299	W	Sharp	--	--	--
1266	W	Sharp	--	--	--
1205	W	Sharp	1210	W	--
1149	M	Sharp	1145	M	Sharp
1123	M	Sharp	--	--	--
1087	M	Sharp	1090	W	--
1047	W	Sharp	--	--	--
1031	W	Sharp	1035	W	--
1010	M	Sharp	1015	W	--
962	W	Broad	960	W	--
877	M	Sharp	--	--	--
830	S	Sharp	840	M	Sharp
800	S	Sharp	--	--	--
740	S	Sharp	750		Broad w/ shoulders
720	S	Sharp	--	S	at 775, 735, 725 &
704	W	Shoulder	--		medium shoulder at 700

TABLE A-23. VERIFICATION OF LC6a
Compound--2,6-Dimethylphenol

Literature Spectrum			Test Mixture Spectrum		
cm ⁻¹	Intensity	Comment	cm ⁻¹	Intensity	Comment
3400	S	Broad			
3040	M	Sharp			
3020	W	Shoulder			
2980	M	Sharp			
2940	M	Sharp	3600-2500	S	Very broad, appears to have peaks at 3100 and 3000.
2910	M	Sharp			
2845	W	Sharp			
2740	W	Sharp			
2640	W	Sharp			
2480	W	Sharp	2480	W	Broad
2400	W	Sharp	--	--	--
1910	W	Sharp	--	--	--
1850	W	Sharp	1850	W	Broad
1780	W	Sharp	--	--	--
1620	W	Sharp	1650-1630	S	Broad
			1610-1570	S	Broad
1600	M	Sharp	1610-1570	S	Broad
1540	W	Sharp	1540	S	Sharp
1480	W	Sharp	1480	W	Sharp
1445	W	Sharp	--	--	--
1430	M	Shoulder	1430	S	Broad
1385	M	Sharp	1375	M	Sharp
1320	M	Broad	--	--	--
1270	M	Sharp	1275	M	Broad
1235	M	Sharp	1235	S	Sharp
1215	M	Sharp	--	--	--
1195	S	Broad	--	--	--
1160	M	Sharp	1160	S	Sharp
1090	M	Sharp	1100	S	Sharp

(continued)

TABLE A-23 (continued)

Literature Spectrum			Test Mixture Spectrum		
cm ⁻¹	Intensity	Comment	cm ⁻¹	Intensity	Comment
1035	M	Sharp	--	--	--
990	W	Sharp	995, 985	S,S	Sharp, sharp
960	W	Sharp	--	--	--
910	M	Sharp	--	--	--
830	M	Sharp	820	W	--
760	S	Sharp	--	--	--
730	S	Sharp	735	S	Sharp
670	W	Broad	--	--	--
640	W	Broad	--	--	--
560	W	Sharp	560	S	Sharp
550	W	Sharp	555	S	Sharp
510	W	Sharp	515	S	Sharp
490	W	Sharp	--	--	--
460	W	Sharp	--	--	--

TABLE A-24. VERIFICATION OF LC6a
Compound--o,6-Biphenol

Literature Spectrum			Test Mixture Spectrum		
cm ⁻¹	Intensity	Comment	cm ⁻¹	Intensity	Comment
3180	S	Broad	3600-2500	S	Very broad, appears to have peaks at 3100, 3000
2950	S	Sharp	3600-2500	S	Very broad, appears to have peaks at 3100 & 3000
2860	S	Sharp	3600-2500	S	Very broad, appears to have peaks at 3100 & 3000
1605	M	Sharp	1610-1570	S	Broad
1570	M	Sharp	1610-1570	S	Broad
1500	S	Sharp	--	--	--
1480	S	Sharp	1480	W	Sharp
1400	S	Sharp	--	--	--
1360	M	Sharp	--	--	--
1300	M	Sharp	--	--	--
1280	M	Sharp	1275	M	Broad
1260	M	Sharp	--	--	--
1250	S	Sharp	1245	S	Sharp
1210	S	Sharp	--	--	--
1200	M	Sharp	--	--	--
1180	M	Sharp	--	--	--
1150	M	Sharp	1160	S	Sharp
1100	M	Sharp	1100	S	Sharp
1070	M	Sharp	--	--	--
1050	M	Sharp	1050	W	--
1010	W	Sharp	1010	M	Sharp
955	W	Sharp	--	--	--
935	W	Sharp	925	M	Broad
860	W	Sharp	850	M	Broad

(continued)

TABLE A-24 (continued)

Literature Spectrum			Test Mixture Spectrum		
cm^{-1}	Intensity	Comment	cm^{-1}	Intensity	Comment
850	W	Shoulder	850	M	Broad
840	M	Sharp	850	M	Broad
820	M	Sharp	820	W	--
770	M	Sharp	780	S	Broad
745	S	Sharp	735	S	Sharp
725	M	Sharp	735	S	Sharp

TABLE A-25. VERIFICATION OF LC6b
Compound--2-Hydroxypyridine

Literature Spectrum			Test Mixture Spectrum		
cm ⁻¹	Intensity	Comment	cm ⁻¹	Intensity	Comment
3080	S	Broad	3600-2500	S	Very broad, appears to have peaks at 3100 & 3000
2950	S	Sharp	3600-2500	S	Very broad, appears to have peaks at 3100 & 3000
2890	S	Sharp	3600-2500	S	Very broad, appears to have peaks at 3100 & 3000
2460	W	Sharp	--	--	--
1840	W	Broad	1850	W	Broad
1680	M	Shoulder	1680	S	Sharp
1610	S	Sharp	1610-1570	S	Broad
1550	S	Broad	1540	S	Sharp
1475	M	Sharp	1480	W	Sharp
1455	M	Sharp	1460	M	Sharp
1380	M	Sharp	1375	M	Sharp
1250	S	Sharp	1245	S	Sharp
1190	W	Sharp	--	--	--
1160	M	Sharp	1160	S	Sharp
1090	M	Sharp	1100	S	Sharp
1010	M	Sharp	1010	M	Sharp
970	M	Sharp	--	--	--
915	M	Sharp	925	M	Broad
880	W	Shoulder	--	--	--
850	W	Sharp	850	M	Broad
780	S	Sharp	780	S	Broad
740	M	Sharp	735	S	Sharp

TABLE A-26. VERIFICATION OF LC6b
Compound--Fluorene-1-Carboxylic Acid

Literature Spectrum			Test Mixture Spectrum		
cm ⁻¹	Intensity	Comment	cm ⁻¹	Intensity	Comment
3080	M	Shoulder	3500-2000	M	Broad
3020	M	Sharp	3500-2000	M	Broad
2670	M	Broad	3500-2000	M	Broad
2440	W	Broad	3500-2000	M	Broad
2350	W	Broad	3500-2000	M	Broad
1900	W	Broad	--	--	--
1690	S	Sharp	1680	S	Broad
1600	W	Sharp	1590	M	Sharp
1490	W	Sharp	1485	W	Shoulder
1435	M	Sharp	1435	M	Sharp
1410	W	Sharp	1415	M	Sharp
1350	W	Sharp	1345	W	Sharp
1320	M	Shoulder	1310	M	Sharp
1305	S	Shoulder	1310	M	Sharp
1280	W	Sharp	--	--	--
1170	W	Sharp	1160	M	Sharp
1160	W	Sharp	1160	M	Sharp
1070	W	Sharp	1065	W	Sharp
1055	W	Sharp	1048	W	Sharp
1015	W	Sharp	1015	W	Sharp
945	W	Sharp	950	W	Shoulder
925	W	Sharp	935	W	Shoulder
910	W	Sharp	914	M	Sharp
880	W	Sharp	873	W	Sharp
820	W	Sharp	817	W	Sharp
750	S	Sharp	750	W	Shoulder
720	W	Sharp	720	W	Shoulder
682	W	Sharp	688	W	Sharp
650	W	Sharp	647	W	Sharp

(continued)

TABLE A-26 (continued)

Literature Spectrum			Test Mixture Spectrum		
cm ⁻¹	Intensity	Comment	cm ⁻¹	Intensity	Comment
630	W	Sharp	630	W	Sharp
590	W	Sharp	580	W	Broad
490	W	Sharp	487	W	Sharp
470	W	Sharp	468	W	Sharp
420	W	Sharp	412	W	Sharp
400	W	Sharp	398	W	Sharp
360	W	Sharp	355	W	Sharp

TABLE A-27. VERIFICATION OF LC6b
Compound--9-Fluorenone-4-Carboxylic Acid

Literature Spectrum			Test Mixture Spectrum		
cm ⁻¹	Intensity	Comment	cm ⁻¹	Intensity	Comment
2950	S	Broad	3500-2000	M	Broad
1740	S	Sharp	--	--	--
1680	S	Sharp	1680	S	Broad
1610	M	Sharp	--	--	--
1580	M	Sharp	1590, 1585	M,M	Sharp, shoulder
1475	S	Broad	1485, 1479	W,M	Shoulder, sharp
1425	M	Sharp	1425	M	Sharp
1400	M	Sharp	1390	W	Sharp
1310	M	Sharp	1310	M	Sharp
1300	M	Sharp	1310	M	Sharp
1290	M	Sharp	--	--	--
1260	M	Sharp	--	--	--
1210	M	Sharp	--	--	--
1195	M	Sharp	1190	M	Sharp
1190	M	Sharp	1190	M	Sharp
1100	W	Sharp	1093	W	Shoulder
1090	M	Sharp	1093, 1085	W,W	Shoulder, sharp
960	W	Sharp	950	W	Shoulder
920	W	Broad	914	M	Sharp
855	W	Sharp	851	W	Sharp
840	W	Sharp	838	W	Sharp
770	W	Sharp	--	--	--
750	M	Sharp	750	W	Shoulder
740	S	Sharp	742	S	Sharp
675	M	Broad	688	W	Sharp

TABLE A-28. VERIFICATION OF LC6b
Compound--2,6-Dimethylphenol

Literature Spectrum			Test Mixture Spectrum		
cm ⁻¹	Intensity	Comment	cm ⁻¹	Intensity	Comment
3400	S	Broad	3650, 3150 3500, 2000	W M	Broad Broad
3040	M	Sharp			
3020	W	Shoulder			
2980	M	Sharp			
2940	M	Sharp			
2910	M	Sharp			
2845	W	Sharp	3500-2000	M	Broad
2740	W	Sharp			
2640	W	Sharp			
2480	W	Sharp			
2400	W	Sharp			
1910	W	Sharp	--	--	--
1850	W	Sharp	--	--	--
1780	W	Sharp	--	--	--
1620	W	Sharp	--	--	--
1600	M	Sharp	1590	M	Sharp
1540	W	Sharp	1550	W	Shoulder
1480	S	Sharp	1485	W	Shoulder
1445	M	Sharp	1449	M	Sharp
1430	M	Shoulder	1425	M	Sharp
1385	M	Sharp	1390	W	Sharp
1320	M	Sharp, broad	1310	M	Sharp
1270	M	Sharp	--	--	--
1235	M	Sharp	--	--	--
1215	M	Sharp	--	--	--
1195	S	Broad	1190	M	Sharp
1160	M	Sharp	1160	M	Sharp
1090	M	Sharp	1093	W	Shoulder

(continued)

TABLE A-28 (continued)

Literature Spectrum			Test Mixture Spectrum		
cm ⁻¹	Intensity	Comment	cm ⁻¹	Intensity	Comment
1035	M	Sharp	1030	W	Sharp
990	W	Sharp	988	W	Shoulder
960	W	Sharp	950	W	Shoulder
910	M	Sharp	905	W	Shoulder
830	M	Sharp	838	W	Sharp
760	S	Sharp	750	W	Shoulder
730	S	Sharp	730	S	Sharp
670	W	Broad	665	W	Sharp
640	W	Broad	647	W	Sharp
560	W	Sharp	--	--	--
550	W	Sharp	545	W	Broad
510	W	Sharp	--	--	--
490	W	Sharp	487	W	Sharp
460	W	Broad	468	W	Sharp

TABLE A-29. VERIFICATION OF LC6b
Compound--Fluoren-9-one

Literature Spectrum			Test Mixture Spectrum		
cm ⁻¹	Intensity	Comment	cm ⁻¹	Intensity	Comment
3400	M	Sharp	3650-3150	W	Broad
			3500-2000	M	Broad
3040	M	Broad	3500-2000	M	Broad
2100	W	Sharp	3500-2000	M	Broad
1950	W	Broad	1950	W	Broad
1860	W	Broad	--	--	--
1820	M	Sharp	--	--	--
1705	S	Sharp	1710	S	Sharp
1680	M	Shoulder	1680	S	Broad
1660	M	Sharp	--	--	--
1635	W	Sharp	--	--	--
1600	S	Sharp	1590	M	Sharp
1580	S	Shoulder	1590, 1585	M,M	Sharp, shoulder
1520	W	Sharp	--	--	--
1480	W	Sharp	1485, 1479	W,M	Shoulder, sharp
1460	M	Sharp	1460	W	Shoulder
1440	S	Sharp	1449	M	Sharp
1360	W	Sharp	1365	W	Shoulder
1290	S	Sharp	--	--	--
1220	W	Sharp	--	--	--
1180	S	Sharp	1190	M	Sharp
1140	M	Sharp	1135	W	Shoulder
1088	S	Sharp	1085	W	Sharp
1045	W	Sharp	1048	W	Sharp
1000	W	Sharp	--	--	--
980	W	Sharp	988	W	Shoulder
935	W	Broad	935	W	Shoulder
910	S	Sharp	914, 905	M,W	Sharp, shoulder
865	M	Sharp	873	W	Sharp

(continued)

TABLE A-29 (continued)

Literature Spectrum			Test Mixture Spectrum		
cm ⁻¹	Intensity	Comment	cm ⁻¹	Intensity	Comment
840	W	Sharp	838	W	Sharp
800	S	Sharp	805	W	Sharp
765	M	Sharp	--	--	--
725	S	Broad	720	W	Shoulder
660	S	Sharp	665	W	Sharp
640	M	Sharp	647	W	Sharp
600	W	Sharp	--	--	--
550	W	Broad	545	W	Broad
495	W	Sharp	500	W	Sharp
465	W	Sharp	468	W	Sharp
430	M	Sharp	435	W	Sharp
395	W	Sharp	398	W	Sharp
380	W	Sharp	--	--	--

TABLE A-30. VERIFICATION OF LC6b
Compound--o-Phenoxybenzoic acid

Literature Spectrum			Test Mixture Spectrum		
cm ⁻¹	Intensity	Comment	cm ⁻¹	Intensity	Comment
3060	M	Sharp			
3040	M	Sharp			
2870	M	Sharp			
2820	M	Sharp	3500-2000	M	Broad
2540	M	Sharp			
2460	W	Broad			
1690	S	Broad	1680	S	Broad
1592	M	Sharp	1590	M	Sharp
1585	M	Sharp	1585	M	Shoulder
1570	M	Sharp	1565	M	Sharp
1478	S	Sharp	1479	M	Sharp
1440	S	Sharp	1449	M	Sharp
1400	M	Sharp	1390	W	Sharp
1300	M	Sharp	1310	M	Sharp
1260	S	Sharp	--	--	--
1235	S	Broad	--	--	--
1190	M	Sharp	1190	M	Sharp
1155	M	Sharp	1160	M	Sharp
1140	W	Sharp	1135	W	Shoulder
1075	M	Sharp	1085, 1065	W,W	Sharp, sharp
1060	W	Sharp	1065	W	Sharp
1010	W	Sharp	1015	W	Sharp
950	W	Broad	950	W	Shoulder
905	W	Shoulder	905	W	Shoulder
895	W	Sharp	905	W	Shoulder
865	M	Sharp	873	W	Sharp
795	W	Sharp	805	W	Sharp
780	W	Sharp	--	--	--
750	M	Sharp	750	W	Shoulder

(continued)

TABLE A-30 (continued)

Literature Spectrum			Test Mixture Spectrum		
cm ⁻¹	Intensity	Comment	cm ⁻¹	Intensity	Comment
730	M	Sharp	730	S	Sharp
680	S	Sharp	688	W	Sharp
640	M	Sharp	647	W	Sharp
620	W	Sharp	630	W	Sharp
570	W	Sharp	580	W	Sharp
525	W	Sharp	--	--	--
475	W	Sharp	468	W	Sharp
335	W	Sharp	--	--	--

APPENDIX B
CONTRACTORS' ASSIGNMENTS OF IR SPECTRAL BANDS

TABLE B-1. SPECTRUM LC4a

Wave numbers cm	Contractor A	Contractor B	Contractor C	Contractor D
3650-3200(W)	3600-3300(W)--OH or NH stretch (Br)	--	3650-3200(W)--H ₂ O in KBr (Br)	3420(W)--OH (Br)
3100-3000(M)	3060(W)--Unsaturated CH	--	3100-3000(W)--Unsaturated CH stretching	3050(W)--Unsaturated CH (anthracene)
3000-2800(W)	2930(W), 2850(W)--Saturated CH	--	3000-2800(W)--Saturated CH (CH ₃ asym. and sym.)	2920(W)--No assignment
2580(W)	2580(W)--SH of mercaption or thiol acid (impurity?)	--	2580(W)--[Instrument artifact]	2580(W)--Aromatic overtone
2000-1700(W)	1780, 1805(W)--C=O of anhydride peroxide (or 1780 peak could be overtone band of 890 cm peak)	--	2000-1700(W)--Summation bands of aromatic (CH) region (multiple, overlapping peaks)	1950(W)--Aromatic overtone 1805(W)--Aromatic overtone 1780(W)--Aromatic overtone 1710(W)--Ester
1700-1600(W-M)	1715(W)--C=O of acid, amide, or ketone	--	1618(W)--v(C-C) of anthracene and of 9,10-dimethylantracene (shoulder)	1690(W)--Ketone 1620(W)--Aromatic, unsaturated C-C (anthracene)
1600-1500(W-M)	1690(W)--C=O of acid, amide, or ketone 1620(W)--Aromatic or heteroaromatic ring stretching	--	1527(W) and 1532(W)--v(C-C) of anthracene and of 9,10-dimethylantracene (Sh)	1530(W)--Aromatic (anthracene)
1500-1400(W-M)	1530(W)--Aromatic or heteroaromatic ring stretching	--	1448(W)--Arom. CH in-plane bend 1408(W)--No assignment	1450(W)--Unsaturated CH (anthracene)
1400-1300(W-M)	1450(W)--Aromatic or heteroaromatic ring stretching	--	1388(W)--Band of 9,10-dimethylantracene 1376(W)--CH ₃ sym. def. (Sh) 1366(W)--Band of 9,10-dimethylantracene	1390(W)--Unsaturated CH 1370(W), 1350(W)--No assignment 1320(W)--(Anthracene)
1300-1200	--	--	1350(W)--No assignment 1318(W)--Anthracene band 1282(W)--No assignment 1272(W)--Anthracene band 1240(W), 1222(W)--No assignment	1270(W)--(Anthracene) 1240(W)--(Anthracene)

(continued)

TABLE B-1. SPECTRUM LC4a (continued)

Wave numbers cm ⁻¹	Contractor A	Contractor B	Contractor C	Contractor D
1200-1100(S,M,W)	1150(M)--CH in-plane bend and benzene ring substitution	--	1182(W)--No assignment 1168(W)--No assignment 1160(W)--No assignment 1150(W)--No assignment 1125(W)--No assignment 1106(W)--No assignment 1076(W), 1068(W), 1053(W), 1038(W)--No assignment 1026(W)--Bend of 9,10-dimethyl-anthracene 999(W)--Anthracene band 978(W)--No assignment 959(M)--Anthracene band 909(W)--No assignment	1180(W)--(anthracene) 1160(W)--No assignment 1150(S)--Fused aromatic rings (anthracene) 1025(W)--Fused aromatic rings (pyrene) 1000(H)--Fused aromatic rings (anthracene) 960(S)--Substituted benzene, fused aromatic rings (anthracene)
1100-1000(W,M)	1000(M)--CH in-plane bend and benzene ring substitution	--		
1000-900(S,M,W)	960(M)--CH in-plane bend and benzene ring substitution	--		
900-800(S,M,W)	890(S)--CH out-of-plane bend and benzene ring substitution	--	887(S)--Anthracene CH out-of-plane bend 861(W), 849(W), 836(W), 825(W)--No assignment 816(W)--CH out-of-plane bend of phenanthrene	885(S)--Substituted benzene, fused aromatic rings (anthracene) 844(M)--Fused aromatic rings (pyrene) 815(M)--Fused aromatic rings
800-700(S,M,W)	750(S), 730(S)--CH out-of-plane bend and benzene ring substitution	Fused ring	778(W), 716(W)--No assignment 752(S), 748(S)--CH out-of-plane bend of 9,10-dimethylanthracene 730(S)--Anthracene CH out-of-plane bend	786(M)--Fused aromatic rings 750(S)--Fused aromatic rings 730(S)--Substituted benzene, fused aromatic rings (anthracene)
700-600(M,W)	600(M)--No assignment	--	628(W), 618(W)--No assignment 603(W)--Band of 9,10-dimethyl-anthracene	--
600-500(M,W)	580(M), 530(M)--No assignment	--	580(W)--Band of 9,10-dimethyl-anthracene 530(W)--No assignment	--

(continued)

TABLE B-1. SPECTRUM LC4a (continued)

Wave numbers cm ⁻¹	Contractor A	Contractor B	Contractor C	Contractor D
500-400(H-W)	475(M), 465(W)--No assignment	--	495(W)--No assignment 475(M)--Out-of-plane ring bend of anthracene 465(W), 440(W), 428(W)--No assignment	--
400-300	390(W)--No assignment	--	393(W), 355(W)--No assignment	--

TABLE B-2. SPECTRUM LC4B

Wave numbers cm ⁻¹	Contractor A	Contractor B	Contractor C	Contractor D
3600-3200(W)	--	--	3600-3200(W)--H ₂ O in KBr (Br)	--
3200-3000(W-M)	3050(M)--Unsaturated CH	--	3050(W), 3020(W), 3000(W)--Un- saturated CH stretch, 3020, 3000 (Sh)	3050(M)--Unsaturated CH
3000-2500(W)	2930(W)--Aliphatic CH 3560(W)--SH of mercaptan or thiol acid	--	2930(W)--Saturated CH CH ₃ asym. stretch 2850(W)--Saturated CH CH ₃ sym. stretch 2560(W)--Instrument artifact	--
2000-1600(W-M)	1620(M)--Aromatic ring stretch	--	1950-1650(W)--Aromatic summation bands; multiple overlapping peaks 1619(W)--Aromatic in-plane ring stretch of anthracene and phenanthrene	1605(W)--Unsaturated CH
1600-1500(W-M)	1530(M), 1500(M)--Aromatic ring stretching	--	1597(W), 1566(W), 1558(W), 1533(W), 1525(W), 1500(W)-- Aromatic in-plane ring stretch of anthracene and phenanthrene	1530(W)--Aromatic (anthra- cene) 1500(W)--Aromatic
1500-1400(W-M)	1450(M)--Aromatic ring stretching	--	1453(W-Sh), 1450(W), 1445 (W-Sh)--CH ₃ asym. bend and aromatic CH in-plane bend	1450(M), 1430(W)--Unsat- rated CH
1400-1300(W)	--	--	1383(W), 1364(W), 1350(W)--CH ₃ sym. bend 1317(W)--Anthracene band 1302(W)--Phenanthrene band	1370(W), 1310(W)--Unsat- rated CH doublet
1300-1200(W)	--	--	1280(W), 1271(W)--No assignment 1243(W)--Phenanthrene band 1235(W), 1225(W), 1201(W-Sh)-- No assignment	1270(W), 1240(W)--Unsat- rated CH

(continued)

TABLE B-2. SPECTRUM 1C4b (continued)

Wave numbers cm	Contractor A	Contractor B	Contractor C	Contractor D
1200-1100(W-M)	1150(M)--CH in-plane bend and benzene ring substitution	--	1169(W)--No assignment 1149(W), 1141(W)--Anthracene and phenanthrene bands	1170(W), 1145(W)--Unsaturated CH
1100-1000(W-M)	1000(M)--CH in-plane bend and benzene ring substitution	--	1091(W)--Phenanthrene band 1070(W), 1038(W), 1025(W)--No assignment	1030(W), 1000(W)--Unsaturated CH (doublet)
1000-900(W-M)	960(M)--CH in-plane bend and benzene ring substitution	--	1000(W)--Anthracene band 960(W)--Anthracene band 951(W)--Phenanthrene band 935(W), 908(W)--No assignment	955(W)--Unsaturated CH (anthracene)
900-800(W-S)	890(S), 820(S)--CH out-of-plane bend and benzene ring substitution	--	888(S)--Anthracene γ (CH) 880(M), 871(W), 835(W) (Sh)--No assignment 821(S)--Phenanthrene γ (CH)	885(S), 820(S)--Substituted benzene-fused aromatic rings
800-700(W-S)	730(S)--CH out-of-plane bend and benzene ring substitution	--	789(W)--No assignment 778(W)--Naphthalene 765(W), 753(W)--No assignment 730(S), 725(M), 715(W)--Anthracene and phenanthrene γ (CH) (Sh)	730(S)--Substituted benzene fused aromatic rings (anthracene)
700-600(W)	--	--	695(W)--Anthracene and phenanthrene 628(W)--No assignment 619(W)--Phenanthrene band 602(W)--Anthracene band	--
600-300(W-M)	475(M), 430(M)--No assignment	--	578(W), 546(W), 530(W)--No assignment 496(W)--Phenanthrene band δ (CC) 475(M)--Aromatic ring out-of-plane bend (anthracene) δ (CC) 441(W)--No assignment 429(W)--Phenanthrene band δ (CC) 393(W), 375(W), 305(W)--No assignment	--

TABLE B-3. SPECTRUM LC5a

Wave Numbers cm ⁻¹	Contractor A	Contractor B	Contractor C	Contractor D
3700-3100(W)	3600-3200(W)--OH or NH stretch-bonded 3410(S)--Probably NH ₂ stretch 3400(M)--Probably NH ₂ stretch/shoulder	--	3700-3100(W)--H ₂ O in KBr (Br) 3420(M)--NH, secondary amine stretching vibration	3410(S)--Aromatic NH
3100-2900(W-M)	3050(M)--Unsaturated CH 2970(M), 2930(W)--Saturated CH, higher CH ₃ content	2970--Aliphatic CH	3045(W)--Unsaturated CH stretch 2975(W), 2930(W)--Saturated CH	3030(M), 2980(M)--Unsatu- rated CH
2900-2800(W)	--	--	2840(W), 2830(W)--Saturated CH stretch	--
2000-1500(W-M)	1930(W), 1890(W), 1860(W), 1770(W)-- Overtone bands of substituted benzene 1650(W), 1680(W)--C=O of amide or con- jugated or hydroxy ketone 1630(H)--NH bend of primary or secon- dary amine 1600(M)--Aromatic ring stretching	--	1900-1650(W)--Aromatic summation bands (orthodisubst. benzene) 1625(W), 1595(W), 1555(W)--Aro- matic in-plane ring stretch of carbazole and substituted carbazoles	1630(M)--Unsaturated CH 1600(S)--Unsaturated CH (NH sub. present) (carbazole)
1500-1400(W-M)	1485(M), 1450(M)--Aromatic ring stretching 1450(H)--CH bend of CH ₃ group	--	1495(W), 1485(M)--Aromatic in- plane ring stretch of carbazole and substituted carbazoles 1470(M)--CH ₃ asym. band 1453(S)--Carbazole in-plane CH bend 1430(W)--No assignment (Sh) 1405(W)--Carbazole bands	1480(S), 1470(S), 1450(S)-- Unsaturated CH (NH sub. present) (carbazole)
1400-1300(W-M)	1380(W)--CH bend of CH ₃ group 1330(S)--Aryl amine or SO ₂	--	1398(W)--Carbazole band 1380(M)--9-ethyl carbazole band 1345(W), 1338(M), 1330(S)--Bands of carbazole and 9-ethyl carbazole 1300(W)--Bands of carbazole	1380(M), 1340(S)--Unsatu- rated CH (NH sub. present) (carbazole)

(continued)

TABLE B-3. SPECTRUM LC5a (continued)

Wave numbers cm ⁻¹	Contractor A	Contractor B	Contractor C	Contractor D
1300-1200(W-S)	1235(S)--C=O of aromatic alcohol or ether	--	1285(W)--Band of carbazole 1240(W)--No assignment, (Sh) 1232(S)--Bands of carbazole and 9-ethyl carbazole 1220(W), 1210(W)--No assignment	1230(S)--Unsaturated CH (NH sub. present) (carbazole)
1200-1100(W-S)	1160(S)--SO ₂ compound 1130(W)--CH in-plane bend and benzene ring substitution	--	1190(W)--No assignment 1156(W)--Bands of carbazole and 9-ethyl carbazole 1140(W)--No assignment, shoulder 1129(W)--Band of 9-ethyl carbazole 1121(W)--Band of 9-ethyl carbazole 1110(W)--No assignment	1155(S), 1130(W)--Unsaturated CH (NH sub. present) (carbazole)
1100-1000(W)	1080(W)--CH in-plane band and benzene ring substitution 1000(W)--CH in-plane band and benzene ring substitution	--	1088(W), 1060(W)--Bands of 9-ethyl carbazole 1020(W), 1010(W), 1000(W)--Bands of carbazole and 9-ethyl carbazole	1000(W)--No assignment
1000-900(W)	930(W)--CH in-plane bend and benzene ring substitution	--	965(W), 960(W)--No assignment 935(W), 930(W)--Bands of carbazole, (Sh)	940(W)--No assignment
900-800(W)	--	--	890(W), 880(W), 865(W), 860(W)--No assignment	--
800-700(W-S)	760(S), 730(S)--CH out-of-plane bend and benzene ring substitution	Hetero fused ring	785(W)--Band of 9-ethyl carbazole 770(W)--No assignment 760(S), 727(S), 723(W)--Out-of-plane CH bend of carbazole and 9-ethyl carbazole	760(S), 730(S)--Fused aromatic rings (carbazole)
700-500(W)	--	--	697(W), 660(W), 630(W), 615(W), 580(W), 560(W), 530(W), 510(W)--No assignments	--
500-400(W)	--	--	475(W), 430(W), 420(W), 490(W)--No assignments, (Br, Sh)	--

TABLE B-4. SPECTRUM LC5b

Wave numbers cm	Contractor A	Contractor B	Contractor C	Contractor D
3700-3100(M-W)	3600-3300(W)--OH or NH stretch-bonded (Br)	--	3700-3150(W)--H ₂ O in KBr (Br)	3500(W)--Water
3100-3000(W)	3050(W)--Unsaturated CH	--	~3050(W)--Aromatic CH stretch	3025(W)--Unsaturated CH
~2500-2600(W)	--	--	~2570(W)--Instrument artifact	--
2000-1600(W)	1675(W)--C=O of amide or quinone or conjugated ketone or C-N of imine	1600(W)--Aromatic	2000-1650(W)--Aromatic summation bands, multiple overlapping peaks	1670(W)--Ketone
	1620(W)--NH bend of primary (M) or secondary (W) amine		1675(W)--ν(C-O) of a quinone (anthraquinone)	1620(W)--Ring breathing
			1660(W)--No assignment	1790(W)--No assignment
			1650(W)--(Sh)	
			1620(W)--In-plane aromatic ring stretch	
1600-1500(M-W)	1585(M), 1515(M)--Aromatic or hetero-aromatic ring stretching	--	1587(W), 1573(W)--In-plane aromatic ring stretch	1510(M)--C-N, (cyclic)-N
			1560(W)--In-plane aromatic ring stretch (Sh)	
1500-1400(W)	1445(W)--Aromatic or heteroaromatic ring stretching	--	1540(W), 1524(W)--In-plane aromatic ring stretch	
	1430(W), 1420(W), 1400(W)--No assignment		1512(M)--Phenazine band	
			1495(W)--Benzo[h]quinoline band	--
			1485(W)--No assignment	
			1470(W)--Phenazine band	
			1460(W)--No assignment	
			1443(W)--Benzo[h]quinoline band	
			1430(W)--Phenazine band	
			1420(W)--No assignment	
			1400(W)--Band of benzo[h]quinoline	
1400-1300(W)	1360(W)--No assignment	--	1390(W), 1350(W)--(Sh)	--
			1360(W)--Phenazine band	
			1335(W), 1305(W)--Anthraquinone band	
			1325(W)--No assignment	

(continued)

TABLE B-4. SPECTRUM LC5b (continued)

Wave numbers cm ⁻¹	Contractor A	Contractor B	Contractor C	Contractor D
1300-1200(W)	1280(W), 1240(W)--Aromatic ether or alcohol	--	1285(W)--Anthraquinone band 1240(W)--No assignment 1230(W)--No assignment (Sh) 1210(W)--Phenazine band	1290(W)--No assignment
1200-1100(W)	1150(W), 1110(W)--CH in-plane bend and benzene ring substitution	--	1190(W), 1148(W)--No assignment 1170(W)--Anthraquinone band 1135(W)--Phenazine band (Sh) 1110(W)--Phenazine band	1150(W)--Ring structures
1100-1000(W)	--	--	1090(W), 1030(W), 1020(W)--No assignment 1060(W)--No assignment (Br, Sh) 1000(W)--Phenazine band	--
1000-900(W)	--	--	965(W)--No assignment (Sh) 960(W), 903(W)--Phenazine band 935(W)--Anthraquinone band	900(W)--No assignment
900-800(M-W)	840(M), 815(M)--CH out-of-plane bend and benzene ring substitution	--	885(W), 860(W), 810(W)--No assignment 800(W)--No assignment (Sh) 840(W)--Band of benzo[h]quinoline [y CH] 822(M)--Aromatic y(CH), phenazine	810(M)--CH deformation in quinoline (doublet) 840(M)--CH deformation in pyridines
800-700(S-W)	750(S)--Out-of-plane bend and benzene ring substitution	800-700--Fused ring	795(W)--No assignment 775(W), 735(W)--No assignment (Sh) 752(S)--Aromatic y(CH), phenazine, and benzo[h]quinoline (Br) 725(W)--Band of benzo[h]quinoline [yCH] (Sh) 700(W)--Anthraquinone band [y(CH)]	750(S)--CH deformation in pyridines

(continued)

TABLE B-4. SPECTRUM LC5b (continued)

Wave numbers cm ⁻¹	Contractor A	Contractor B	Contractor C	Contractor D
700-600(W)	--	--	675(W), 620(W)--No assignment 660(W)--Phenazine band 630(W)--No assignment (Sh)	--
600-500(W)	--	--	595(W)--Phenazine band 575(W), 545(W), 530(W)--No assignment	--
500-400(W)	--	--	495(W), 450(W), 425(W), 410(W)--No assignment 480(W)--No assignment (Br, Sh)	--
400-300(W)	--	--	395(W)--No assignment	--

TABLE B-5. SPECTRUM 1C6a

Wave numbers cm ⁻¹	Contractor A	Contractor B	Contractor C	Contractor D
3700-3100	3600-3350(W)--OH or NH unbonded stretch, shoulder 3350-2400(S)--OH-O bonded stretch/(Br)	--	3700-3100(W)--H ₂ O in KBr, (Br) 3600-2200(M)--NH stretch, acidic, H bonded, (Br)	3120(S)--OH, CH, (Br)
2600-2400(W)	2580(S)--SH of mercaptan or thiol acid/impurity	--	~2580(W)--Instrument artifact 2480(W)--No assignment	--
1900-1600(W-M)	1680(S)--C=O of conjugated ketone or aryl acid or C=O of ortho-OH or -NH ₂ of aromatic ester or C=N of imine 1650(S)--C=O of ortho-OH or -NH ₂ aromatic ketone or acid or C=O amide I band or C=O of quinone or C=C alkene 1600(S)--Aromatic or heteroaromatic ring stretching	--	1668(M)--No assignment 1640(S)--v(C-O) of pyridine form, (Br)	1650(S)--CO, aromatic C-O, (Br) 1600(S)--CO, aromatic C-O
1600-1500(W-S)	1580(S), 1540(M)--Aromatic or heteroaromatic ring stretching or amide II band of secondary amide	--	1590(S), 1540(M), 1510(W)--Aromatic ring stretch	--
1500-1400(W-M)	1480(W), 1460(W)--Aromatic ring stretching 1430(M)--CH ₂ near S, P, Si or C-O or heteroaromatic ring stretching, e.g., 2-substituted pyridine	--	1482(W), 1465(W)--No assignments 1455(M), 1430(M)--In-plane aromatic ring bend	1430(M)--No assignment
1400-1200(W)	1240(M)--C-O of aromatic alcohol or ether	--	1384(W), 1370(W), 1350(W-Sh), 1340(W-Sh), 1325(W), 1295(W), 1278(W), 1243(W), 1233(M), 1220(W)--No assignments	1245(M)--Aromatic -C-O
1200-1000(W-M)	1160(S), 1100(M)--No assignment 1010(M)--CH in-plane bend and benzene ring substitution	--	1172(W-Sh), 1159(M), 1100(W), 1048(W), 1040(W), 1010(W)--No assignments	1160(S)--No assignment 1100(M)--Aromatic rings
1000-900(W-M)	980(M), 995(M)--CH in-plane bend and benzene ring substitution	--	995(W), 985(M), 965(W-Sh), 925(W), 900(W-Br)--No assignments	980(M), 925(W)--No assignments

(continued)

TABLE B-5. SPECTRUM LC6a (continued)

Wave numbers cm ⁻¹	Contractor A	Contractor B	Contractor C	Contractor D
900-700(W-M)	780(S), 730(W)--CH out-of-plane bend and benzene ring substitution	--	860(W-Sh), 848(W), 822(W), 815(W)--No assignments 782(M), 770(M), 760(W), 730(W)-- Aromatic γ (CH) 720(W-Sh)--No assignment	785(S), 730(S)--Fused rings
700-500(W-M)	620(M), 560(M)--No assignments 530(M)--No assignment	--	618(W), 560(W), 555(W), 528(W), 515(W)--No assignments	--
500-300(W-M)	475(M)--No assignment	--	490(W)--No assignment 475(M)--Aromatic out-of-plane ring bend 465(W-Sh), 450(W-Sh), 435(W-Sh), 392(W)--No assignments	--

TABLE D-6. SPECTRUM LC6b

Wave numbers cm	Contractor A	Contractor B	Contractor C	Contractor D
3700-1900(M-W)	3600-3300(W)--OH or NH unbonded stretch (Br) 3300-2400(W)--OH...O bonded stretch (Br) 2580(W)--SH of mercaptan or thiol acid (impurity?) 2650(W), 2350(W)--Unassigned	--	3650-3150(W)--H ₂ O in KBr (Br) 3500-2000(M)--OH, acidic, COOH (Br) ~2580--Instrument artifact 1950(W)--Aromatic summation band (Br)	3450(W)--OH (water) (Br) 3000(W)--CH (Br)
1800-1700(S)	1710(S)--C=O of acid, aldehyde, ketone or conjugated or aromatic ester	--	1710(S)--ν(C=O), ketone	1700(S)--C=O, ketone
1700-1600(S)	1680(S)--C=O of conjugated ketone, quinone or aryl acid or ortho- OH or -NH ₂ aromatic ester or C-N of imine	--	1680(S)--ν(C=O), COOH (Br)	--
1600-1500 (M-W)	1600(M), 1560(M)--Aromatic ring stretching or NH bend of primary amine	--	1590(M)--Aromatic in-plane stretching bands 1585(M)--Aromatic in-plane stretching band (Sh) 1565(M)--Aromatic in-plane stretching band 1550(W)--Aromatic in-plane stretching band (Sh)	1600(S)--Unsaturated CH
1500-1400(S, M, W)	1480(M), 1450(M)--Aromatic ring stretching 1430(W)--CH ₂ near S, P, Si, or C=O; heteroaromatic ring stretching	--	1479(M)--Aromatic in-plane stretching bands 1485(W)--Aromatic in-plane stretching band (Sh) 1449(M)--CH, in-plane bend 1460(W)--CH, in-plane bend (Sh) 1425(M)--OH def. of COOH, in-plane 1415(M)--No assignment	1450(S)--Unsaturated CH
1400-1300	1300(S)--Aryl amine	--	1390(W), 1378(W), 1345(W), 1310(M)--No assignment 1365(W)--No assignment (Sh)	1300(S)--C-O-C, aromatic substituted

(continued)

TABLE B-6. SPECTRUM LC6b (continued)

Wave numbers cm ⁻¹	Contractor A	Contractor B	Contractor C	Contractor D
1300-1200(M-S)	1240(S)--C-O of aromatic ester, alcohol or ether	--	1290(S)--C-O stretch of COOH 1270(M)--No assignment 1285(M)--No assignment (Sh) 1238(M)--No assignment (Br)	1240(S)--C-O-C, cyclic ether
1200-1100(M-W)	1190(W), 1160(W)--CH in-plane bend and benzene ring substitution	--	1190(W), 1160(M)--No assignment 1135(W), 1115(W)--No assignment (Sh)	1190(M), 1160(M)--C-O-C, cyclic ether (xanthone)
1100-1000(W)	1085(W)--CH in-plane bend and benzene ring substitution	--	1093(W)--No assignment (Sh) 1085(W), 1065(W), 1048(W), 1030(W), 1015(W)--No assignment	--
1000-900(M-W)	915(M)--CH out-of-plane bend and ben- zene ring substitution	--	988(W), 950(W), 935(W), 905(W)--No assignment (Sh) 914(M + Br [W] component)--Br component is OH out-of-plane bend of COOH	910(M)--Cyclic ether
900-800(M)	870(M)--CH out-of-plane bend and ben- zene ring substitution	--	873(W), 851(W), 838(W), 817(W), 805(W)--No assignment	875(M)--fused rings
800-700(M,W,S)	750(M)--CH out-of-plane bend and ben- zene ring substitution	--	750(W), 720(W)--No assignment (Sh) 742(S), 730(S)--Aromatic γ (CH)	740(S)--Substituted rings (doublet)
700-600	--	--	688(W), 665(W), 647(W), 630(W)--No assignment	--
600-500	--	--	500(W)--No assignment 580(W), 545(W)--No assignment (Br)	--
500-400(W)	--	--	487(W), 468(W), 450(W), 435(W), 412(W)--No assignment	--
400-300	--	--	398(W), 355(W)--No assignment	--

TABLE B-7. SAMPLE 1C5

Wave numbers cm	Contractor A	Contractor B	Contractor C	Contractor D
3600-3100(W)	OH, NH stretch (Br)	--	3600-3100(W)--H ₂ O in KBr	3400(M-S)--O-H (Br)
3100-3000(W)	3050--Unsaturated CH stretch	3060, 3030--Aromatic CH	3100-3000(W)--Aromatic CH stretch (unresolved)	3060(M-S)--Phenyl-H sharp/ quinoline and acridine
2000-3000	--	--	--	2975, 2950, 2910(W)--C-H, CH ₃ -CH ₂
2000-1700(W)	--	--	2060-1700(W)--Aromatic summation bands; multiple overlapping peaks	2340, 2240--(C-C)
1674(W)	1670(W)--C=O conjugated ketone	1698--No assignment	1674(W)--v (C=O) of a quinone	--
1655-1660(W)	C=C of alkene, C=O of amide (M)	--	1655-1660(W)--Ring stretch of acridine	-C-O (Br)
1620-1630(W)	--	1620--No assignment	1628(W)--Phenazine band	1620(M)--C-C
1610-1619(W)	1610--Aromatic or heteroaromatic ring stretch	--	1614(W)--Ring stretch, 1,10-phe- nanthrolone and benzo[h]quino- line	--
1590-1600(W)	--	1590(M)--No assignment	1597, 1593--Ring stretch, 2,6- dimethylquinoline	1600, 1590(M-S)--C-C (con- jugated), Phenyl-N, C-N (indicates subst. quino- line)
1580-1590(W)	1585(W)--Aromatic or heteroaromatic ring stretch	--	1588(W)--Ring stretch, anthra- quinone	--
1560-1570(W)	--	1560(W)--No assignment	1580(W)--Ring stretch, 1,10-phe- nanthrolone	1560--(Phenyl-M)
1549-1559(W)	1555(W)--Aromatic or heteroaromatic ring stretch	--	1568, 1565--Ring stretch, 1,10- phenanthrolone	--
1500-1510(M)	1505(W)--Aromatic or heteroaromatic ring stretch	1508(M)--No assignment	1555(W)--Ring stretch, 2,6- dimethylquinoline and acridine 1549(W)--Ring stretch, phenazine	--
			1509(W)--Ring stretch, phenazine acridine	1510(S)--C-N-C

(continued)

TABLE B-7. SAMPLE LCS (continued)

Wave numbers cm ⁻¹	Contractor A	Contractor B	Contractor C	Contractor D
1490-1499(M-W)	--	--	1499(M)--Ring stretch, 1,10-phenanthroline 1490(W)--Ring stretch, 2,6-dimethylquinoline	--
1470-1475(W)	--	--	1473(W)--No assignment	1475(W)--Phenyl substituted
1460-1469(W)	--	--	1467(W)--Phenazine and anthraquinone	--
1450-1459(W)	--	--	1459(W)--Acridine	--
1440-1459(W)	--	1445(M)--No assignment	1440(W)--Benzo[h]quinoline and 2,6--dimethylquinoline	1445(M)--Phenyl substituted
1420-1430(W)	--	--	1426(W)--Phenazine	1430(W-M)--C-M 1420(S)--Phenyl substituted
1410-1419(M)	1410(S)--CH ₂ next to C=O CH of cis-disubstituted olefin	1417(M)--No assignment 1410(M-M)--No assignment	1412(M)--No assignment	--
1400-1409(M)	--	--	--	1405(M)--Phenyl substituted
1390-1399	--	--	1397(W)--Acridine 1391(W)--2,6-Dimethylquinoline	--
1360-1375(W)	--	1362(W)--No assignment	1375(W)--2,6-Dimethylquinoline 1365(W)--2,6-Dimethylquinoline	--
1350-1360(W)	1355(W)--No assignment	--	1355(W)--Phenazine	1360(W-M)--C-O
1340-1349(W)	--	--	1346(W)--1,10-Phenanthroline	1340(W-M)--C-O
1330-1339(W)	--	1333(W)--No assignment	1335(W)--2,6-Dimethylquinoline	1330(W-M)--C-O
1327(W)	--	--	1327(W)--Anthraquinone	--
1300-1320(W)	1310(M)--N- ϕ of aromatic secondary amine	1305(W)--No assignment	1316(W)--No assignment 1300(W)--Anthraquinone	1315(W)--C-O
1280-1290(W)	1280(W)--No assignment	1285(W)--No assignment	1280(W)--Anthraquinone	1285(W)--C-O
1260-1270(W)	--	--	1261(W)--2,6-Dimethylquinoline	1270(W)--C-O

(continued)

TABLE B-7. SAMPLE LCS (continued)

Wave numbers cm ⁻¹	Contractor A	Contractor B	Contractor C	Contractor D
1210-1220(W)	--	1220(W)--No assignment	1214(W)--2,6-Dimethylquinoline	1220(W)-- -C=O, Phenyl-OH 2210(W)-- -C=O
1200-1205(W)	--	--	1201(W)--Phenazine band	--
1180-1190(W)	--	--	1190(W), 1180(W)--No assignment	1190(WV)-- -C=O
1160-1179(W)	--	--	1173(W)--No assignment 1165(W)--Anthraquinone band	1170(WV)--C-N-C
1140-1159(W)	--	1140(W)--No assignment	1145(W)--No assignment 1140(W)--Phenazine and acridine	1140(W)--C-N-C
1120-1139(W)	1130(W)--CH of aromatic ring; in-plane	--	1131(W)--Partly 1,10-phenanthroline 1125(W)--No assignment	--
1100-1110(W)	--	1115(W)--No assignment	1110(W)--Partly 2,6-dimethylquinoline 1102(W)--Phenazine	1110(W)--C-N-C
1080-1100(W)	1085(W)--CH of aromatic ring; in-plane	1093(W)--No assignment	1087(W)--1,10-Phenanthroline	1094(W)-- C-N-C, Ph-OH 1080(W)--C-C
1060-1070(W)	--	--	1070(W)--1,10-Phenanthroline 1060(W)--No assignment	--
1030-1040(W)	--	1033(W)--No assignment	1032(W)--1,10-Phenanthroline and 2,6-dimethylquinoline	1030(W)--C-C
1010-1029(W)	--	1020(W)--No assignment	1026, 1010(W)--No assignment	1020(W)--C-C
990-1000(W)	--	996(W)--No assignment	995(W)--Acridine 990(W)--Phenazine	995(W)--C-C
980-989(W)	--	--	983, 980(W)--No assignment	--
950-970(W)	--	956(W)--No assignment	970(W)--Acridine 950(W)--Phenazine	959(W)--Phenyl C=O
900-930(W)	--	938(W)--No assignment	929(W)--Anthraquinone 905(W)--Acridine	935(W)--C-C 905(W)--C-C

(continued)

TABLE B-7. SAMPLE LCS (continued)

Wave Numbers cm	Contractor A	Contractor B	Contractor C	Contractor D
870-899(W)	--	892(W)--No assignment	897(W)--Phenazine and 2,6-dimethylquinoline 874(W)--Benzo[h]quinoline	870(W)--Substituted phenyl
850-669(W)	--	--	869(W)--No assignment 850(W)--Phenazine and 1,10-phenanthroline	--
810-840(M)	830(M)--CH of aromatic ring	840(M)--No assignment 822(M)--No assignment 815(W)--No assignment	832(M)--2,6-Dimethylquinoline and benzo[h]quinoline 813(M)--Phenazine, v(CH)	835(S)--Substituted phenyl 820(S)--Substituted phenyl
780-810(W)	--	--	800(W)--Benzo[h]quinoline and anthraquinone, v(CH) 781(W)--Phenazine	805(M)--Substituted phenyl
750-770(W)	--	--	763(W)--Phenazine 752(W)--2,6-Dimethylquinoline	--
740-749(S)	740(S)--CH of aromatic ring; out-of-plane wag	745(S)--No assignment	747(S)--Phenazine, v(CH) 743(S)--Acridine, v(CH)	740(doublets)--Substituted phenyl
720-739(S)	--	730(S)--No assignment	739(S)--Phenazine, v(CH) 729(M)--1,10-Phenanthroline, v(CH)	720(M)--C-C ring
700-719(W)	--	--	717(W)--1,10-Phenanthroline and benzo[h]quinoline, v(CH) 700(W)--1,10-Phenanthroline, v(CH)	705(W)--Ring-C-C 700(W)--Metal ring
680-699(W)	--	695(M)--No assignment	693(W)--No assignment 688(W)--Anthraquinone, v(CH)	--
650-679(W)	--	--	659(W)--No assignment	650(W)--Phenyl ring
640-649(W)	--	--	649(W)--Phenazine and 2,6-dimethylquinoline 645(W)--No assignment	--

(continued)

TABLE B-7. SAMPLE LC5 (continued)

Wave numbers cm ⁻¹	Contractor A	Contractor B	Contractor C	Contractor D
600-630(W)	--	622(W)--No assignment	614(W)--1,10-Phenanthroline 609(W)--Acridine	615(W)--Phenyl ring
560-590(W)	590--No assignment	--	583(W)--Phenazine 581(W)--No assignment	590(S)--Phenyl ring
370-559(W)	--	--	532, 481(W)--2,6-Dimethylquinoline 462(W)--Phenazine and acridine 441(W)--2,6-Dimethylquinoline 415(W)--No assignment 400(W)--1,10-Phenanthroline 396(W)--2,6-Dimethylquinoline 388(W)--No assignment 381(W)--Phenazine and anthraquinone 373(W)--Acridine	--

TABLE B-8. SAMPLE IC6

Wave numbers cm ⁻¹	Contractor A	Contractor B	Contractor C	Contractor D
3650-3250(W)	3300-2400(W)--OH stretch + OH...O of carboxylic acid/weak, multiple peaks	--	H ₂ O in KBr 3413(W)--Overtone of carbonyl at 1715 cm ⁻¹	3410(W)--NH (free NH, amide)
3250-2200(W)	2400(W)--OH stretch + OH...O of carboxylic acid/weak, multiple peaks	--	3250-2200(W)--Carbonyl OH stretch of 9-F-4-CA and 9-F-2-CA	3000(S)--Acid OH and N ⁺ -H 2680, 2580(M)--CH (saturated)
2000-1750(W)	--	--	Aromatic summation bands; multiple overlapping peaks	--
1700-1749(S)	1710(S)--C=O of acid	1720(S)--No assignment	1715(S)--Ketone v(C=O) of 9-F-4-CA, 9-F-2-CA, and 9-F	1700(S)--C-CO ₂ H
1680-1699(M)	1680(S)--C=O of singly conjugated ketone or ortho-amino substituted aromatic acid	1683(S)--No assignment	1683(M)--Acid v(C=O) of 9-F-4-CA and 9-F-2-CA	--
1660(M)	--	--	No assignment	--
1600-1630(W-M)	1600(W)--Ring stretching	1605(M)--No assignment	1622(W)--Ring stretch of 9-F-4-CA 1609(M)--Ring stretch of 9-F-2-CA and 9-F	1610(S)--Doublet C-C, NH amide
1580-1599(W-M)	--	--	1598(M)--Ring stretch of 9-F 1587(W)--Ring stretch of 9-F-4-CA and 9-F-2-CA	--
1560-1579(S-M)	1565(M)--Ring stretching(?)	1573(M)--No assignment	1568(W)--Ring stretch of 9-F-4-CA and 9-F-2-CA	1570(S)--C-NH, -CO ₂
1470-1489	1470(W)--Ring stretching	1477(W)--No assignment	1486(W)--No assignment 1472(M)--Band of 9-F-4-CA and 9-F-2-CA	1470(M-S)--Amine-NH
1450-1469(W)	--	1468(W)--No assignment	1463(W)--Band of 9-F-4-CA and 9-F-2-CA	1455(S)--Phenyl-substitution
1430-1449	--	--	1449(W)--Band of 9-F 1439(W)--Band of 9-F-4-CA and 9-F-2-CA	1430(S)--Phenyl-substitution, CH ₃

(continued)

TABLE B-8. SAMPLE LC6 (continued)

Wave numbers cm ⁻¹	Contractor A	Contractor B	Contractor C	Contractor D
1400-1429(W)	1415(W)--OH bend, -acid	1423(W)--No assignment	1422, 1418(W)--Band of 9-F-4-CA and 9-F-2-CA	--
1380-1399(W)	--	1392(W)--No assignment	1390(W)--Band of 9-F-4-CA and 9-F-2-CA	1395(W-M)--CO ₂
1360-1379(W)	--	--	1374(W)--Band of 9-F 1363(W)--Band of 9-F-4-CA and 9-F-2-CA	1370(W)--CO ₂
1340-1359(W)	--	--	1347(W)--No assignment	1350(W-M)--CO ₂
1300-1339(M)	1305(M)--C-O stretch, -acid	1315, 1300(M)--No assignment	1311(M)--Band of 9-F-4-CA	1300(S doublet)--C-C-M, AMID
1280-1299(M-W)	1295(M)--C-O stretch, -acid	1280(W)--No assignment	1298(W)--Band of 9-F-2-CA and 9-F	1280(M-S)--C-O
1260-1279(W)	1270(W)--No assignment	--	1286(W)--No assignment	1275(M-S)--C-
1240-1259(W)	1240(W)--In-plane ring CH bending	1245(W)--No assignment	1279(W)--Band of 9-F-4-CA 1260(W)--Band of 9-F-2-CA	1250(M-S)--C-CO ₂
1170-1200(W)	--	1193(W)--No assignment	1241(W)--Band of 9-F-4-CA 1189(W)--Band of 9-F-4-CA and 9-F	1195(M-S)--C-CO ₂ , -C-O
1140-1169(W)	1160(W)--In-plane ring CH bending	1150(W)--No assignment	1178(W)--Band of 9-F-4-CA 1161(W)--Band of 9-F-4-CA 1147(W)--Band of 9-F-4-CA and 9-F	1152(M-S)--C-O
1080-1099(W)	1080(W)--In-plane ring CH bending	1090, 1082(W)--No assignment	1092(W)--Band of 9-F 1089(W)--Band of 9-F-4-CA	1090(S)--C-M-C, ring structure 1082(S)--C-M-C, ring structure
1060-1079(W)	--	--	1078(W)--Band of 9-F-4-CA 1067(W)--No assignment	1070(W)--Ring, absorptions
1000-1059(W)	--	--	1050, 1025, 1009(W)--Band of 9-F-4-CA	1055, 1014(W)--Ring, absorptions

(continued)

TABLE B-8. SAMPLE LC6 (continued)

Wave numbers cm	Contractor A	Contractor B	Contractor C	Contractor D
970-999(W)	--	--	988, 976(W)--Band of 9-F-4-CA	985(W)--(Doublet), ring, absorptions
930-969(W)	960(W)--OH-O bend of carboxyl dimer	960, 938(W)--No assignment	954, 933(W)--Band of 9-F-4-CA	960, 938(W-S)--M containing rings
900-929(W)	--	918(W)--No assignment	913(W)--Band of 9-F-4-CA and 9-F	920(S)--Phenyl-C-OH, acidic OH
850-899(W)	--	860(W)--No assignment	852(W)--Band of 9-F-4-CA 885(W)--Band of 9-F-4-CA and 9-F	890, 855(M)--Ph-substituted
800-849(W)	--	835(W)--No assignment	828(W)--Band of 9-F-4-CA 815(W)--No assignment 808(W)--Band of 9-F	830(W)--Phenyl-substituted 810(M-S)--Phenyl-substituted rings
750-799(W)	--	770(W)--No assignment	792(W)--Band of 9-F-4-CA 770(W)--Band of 9-F-4-CA and of 1 - P(?) 762(W)--Band of 9-F-4-CA	770(M doublet)--Phenyl-substituted rings
700-749(W)	730(S)--Out-of-plane ring CH bending	747(W), 735(S)--No assignment	742(M), 729(S)--Band of 9-F-4-CA, 9-F-2-CA, and 9-F, γ (CH)	740(S doublet) Imadazole ring, out-of-plane H bend
650-699(W)	--	670, 650(W)--No assignment	686(W)--No assignment 667(W)--Band of 9-F 664(W)--Band of 9-F-4-CA	690(W-M), 668(S), 650(W-M)--Substituted rings
600-649(W)	--	635(W)--No assignment	645(W)--Band of 9-F 622(W)--Band of 9-F-4-CA 609(W)--No assignment	630(W-M)--Substituted rings
550-599(W)	--	--	587(W)--Band of 9-F-4-CA 554(W)--No assignment	590(W-M)--Substituted rings
500-549(W)	--	--	545, 538(W)--Band of 9-F-4-CA	545(M)--Substituted rings

(continued)

TABLE B-8. SAMPLE LC6 (continued)

Wave numbers cm	Contractor A	Contractor B	Contractor C	Contractor D
400-499(W)	--	--	492, 483(W)--Band of 9-F-4-CA 445, 429(W)--Band of 9-F-4-CA and 9-F	--
350-399(W)	--	--	396, 350(W)--Band of 9-F-4-CA 9-F-4-CA-9-Fluorenone-4-car- boxylic acid 9-F-2-CA-9-Fluorenone-2-car- boxylic acid 1-P-1-Phenalenone 9-F-9-Fluorenone	--

TABLE B-9. COAL TAR SAMPLE LC FRACTION 4

Wave numbers cm ⁻¹	Contractor A	Contractor B	Contractor C	Contractor D
3700-3000(S)	3600-3100(W)--OH, NH stretch (3400 cm ⁻¹ peak) 3050(W)--Unsaturated CH stretch	3052(W)--OH stretch	H ₂ O in KBr + a/c v(OH)	3380(W)--OH 3050(W)--Phenyl-H
2900-3000(M)	2950, 2925(S)--Saturated CH stretch	2955(M)--CH ₂ , CH ₃ stretch 2922(S)--CH ₂ , CH ₃ stretch	2925(W)--CH ₂ antisym. stretch 2960(W)--CH ₃ antisym. stretch	2950(W)--CH ₃ 2910(S)--CH ₂
2800-2900(M)	2850(S)--Saturated CH stretch	2850(M)--CH ₂ , CH ₃ stretch	2865(W)--CH ₃ sym. stretch 2853(W)--CH ₂ sym. stretch	2850(W)--CH ₂
2200-2250(W)	2225(W)--C-N	2228(W)--No assignment	--	2220(W)--C-stretch
1800-1600(W-M)	1720(W)--C=O of conjugated ester, aliphatic aldehyde or dialkyl ketone 1695(W)--C=O of acid, ketone, aldehyde 1600(W)--C-O--HO hydrogen bonded ketone and/or aromatic C-C with O substituent	1698(M)--No assignment 1605(M)--C-C, C-N	1737(W)--v(C-O), ester? 1625(W)--H ₂ O in KBr	1695(W)--C-O 1660(W)--C=O 1600(W)--C-C-
1500-1300(M)	1485(W)--Ring stretching 1450(M)--CH ₂ , CH ₃ , aromatic C=C 1375(W)--CH ₃ 1320(W)--C-O of α , β unsaturated ester	1490(W)--No assignment 1460(M)--CH ₂ bend 1450(M), 1325(W)--No assignment 1375(W)--CH ₃ bend	1435(W)--CH ₂ bend and CH ₃ asym. bend 1379, 1370(M)--CH ₃ sym. bend	1490(M)--CH ₂ 1450(S), 1375(M)--CH ₃ 1320(W)--Phenyl-O
1300-1100(M)	1230(W)--C-O of α , β unsaturated ester, aryl ether or alcohol 1280(W)--C-O of aromatic alcohols	1270--No assignment 1235(M), 1200(W)--No assignment	1150(M)--v(C-O)? + C-OH 1105(S)--v(C-O)? C-OH	1275(W)--Phenyl-OH, C-O, -C 1235(W)--Phenyl-OH 1210(M)--Phenyl-O
1100-1000(S)	1000(W)--C-O of aromatic alcohols or CH in-plane ring stretch	--	1050(S)--v(C-O)? CH ₂ OH 1020(S)--v(C-O)? CH ₂ OH	1030(W)--Phenyl rings
1000-800(M)	875, 800(W)--C-H out-of-plane ring stretch	880, 800(W)--No assignment	990(M)--No assignment	950(W)--CH-CH 810(W)--Substituted phenyl
800-400(M)	740(W)--CH out-of-plane ring stretch	770--No assignment 750, 730(M)--fused ring	800-400--Multiple overlapping peaks	750(M)--Substituted phenyl 695(M)--Phenyl ring

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TABLE B-10. COAL TAR SAMPLE LC FRACTION 5

Wave numbers cm	Contractor A	Contractor B	Contractor C	Contractor D
3600-3100(M)	3600-3100(W)--OH, NH stretch, phenols	3400(M)--OH stretch	3630-3650(W)--No assignment 3650-3150(S)--H ₂ O in KBr	3350(W)--OH
3100-2900(M)	2955, 2925(S)--Saturated CH ₃ , CH ₂	3040(W)--Aromatic CH stretch 2955, 2922(S)--CH ₂ , CH ₃	2955(W)--CH ₃ antisym. stretch 2925(S)--CH ₂ antisym. stretch	2960(W)--CH ₃ 2925(S)--CH ₃
2900-2800(M)	2860(S)--Saturated CH ₃ , CH ₂	2860(M)--CH ₂ , CH ₃ stretch	2865(M)--CH ₃ sym. stretch 2853(M)--CH ₂ sym. stretch	2850(M)--CH ₂
1800-1500(M)	1725(W)--C=O of conjugated ester, aliphatic aldehyde or dialkyl ketone 1695(M)--C=O of acid, ketone, aldehyde 1600(S)--C=O--HO and/or aromatic C=O with 0 substituent 1500(W)--Ring stretching	1690, 1660, 1595(W)--No assignment	1685(W)--v(C=O), conjugated ketone? amide? aromatic acid? 1618(M)--H ₂ O in KBr 1600(M)--Aromatic ring stretch	1685(M)--C=O 1600(S)--C=O 1500(M)--CH ₂
1500-1200(M-W)	1450(M)--CH ₂ , CH ₃ ; aromatic C-C 1375(W)--CH ₃	1490--No assignment 1450(M)--CH ₂ bend 1375(W)--CH ₃ bend 1270(M), 1235, 1210--No assignment	1448(M)--CH ₂ bend and CH ₃ antisym. bend 1370(W)--CH ₃ sym. bend 1260(W)--No assignment	1450(S), 1375(M)--CH ₂ 1270(M-S)--Phenyl-OH; C-O 1215(S)--Phenyl-O
1200-900(W)	1110(M)--C=O of aromatic alcohols or CH in-plane ring stretch	1190(M), 1030(W), 995(W)--No assignment	--	1120(W)--Phenyl ring 1030(W)--Phenyl ring 950(W)--CH-CH
900-700(W)	875, 800(W)--CH of meta and para substituted aromatic 750(W)--CH of ortho substituted aromatic	815(W), 780(W), 750(M)--No assignment	740(M)--v(CH) of aromatic	830, 810, 750(M)--Substituted phenyl ring
695(W)	--	695(W)--No assignment	--	695(W)--Substituted phenyl ring

TABLE B-11. COAL TAR SAMPLE LC FRACTION 6

Wave numbers cm ⁻¹	Contractor A	Contractor B	Contractor C	Contractor D
3700-3000(M)	3600-3100(M)--OH, NH stretch, phenols 3050(W)--Unsaturated CH	3320(M)--OH stretch 3055(W)--Aromatic CH	3700-2200(M)--v(OH) of H ₂ O, alcohol, or phenol, COOH 3100-3000(W)--Aromatic CH stretch	3250(M)--OH 3050(W)--Phenyl-H
3000-2900(W)	2955, 2920(S)--Saturated CH ₃ , CH ₂	2955(W)--CH ₂ , CH ₃ stretch	2955(M)--CH ₃ antisym. stretch 2923(S)--CH ₂ antisym. stretch	2960(W)--CH ₃ 2920(S)--CH ₂ 2850(M)--CH ₂
2900-2000(W)	2800-2350(W)--OH·O strongly hydrogen bonded 2850(S)--Saturated CH ₃ , CH ₂	2870--CH ₂ , CH ₃ stretch 2850(M)--CH ₂ , CH ₃ stretch	2870(M)--CH ₂ sym. stretch 2853(M)--CH ₂ sym. stretch	
1700-1500(W)	1690(M)--C=O of acid, ketone, aldehyde 1595(S)--C=O·HO and/or aromatic C-C with O substituent 1500(W)--Ring stretching	1680(M)--No assignment 1590(S)--Amine 1510(M)--No assignment	1685(M)--v(C=O), probably aromatic acid 1598(S)--Aromatic ring stretch, phenols 1506(M)--Aromatic ring stretch, phenols	1700(M)--C=O 1600(S)--C-C- 1500(W)--CH ₂ , C-N-C
1500-1400(W)	1450(M)--CH ₂ , CH ₃ ; aromatic C-C	1455(W)--CH ₂ bend	1485(M)--Aromatic ring stretch, phenols 1460(M)--CH ₃ antisym. bend + CH ₂ bend 1448(S)--CH ₃ antisym. bend + CH ₂ bend	1450(S)--CH ₃
1400-1300(W)	1375(W)--CH ₃ bend	1375(W)--CH ₃ bend	1373(M)--CH ₃ sym. bend 1350(M)--Band of phenols, β(OH)	1375(M)--CH ₃
1300-1000(W)	1310-1110(M)--C-O of aromatic alcohols 1180, 1165, 1035(W)--No assignment	1265(M)--Amine 1235(M)--Phenol 1180, 1165, 1035(W)--No assignment	1265(S), 1220(S)--Band of phenols, v(C-O) 1030(M)--v(C-O), CH ₂ OH ?	1270(M)--C-O, C-O, Ph-OH 1230(M)--Phenyl-OH 1035(M)--Phenyl ring
1000-800(W)	830(W)--CH of para substituted aromatic	880, 830, 815(W)--No assignment	950, 870(W)--No assignment 826(W)--v(C-H, p-cresol 809(W)--Band of phenol	820(M)--Substituted phenyl
800-600(W)	745(W)--CH of ortho substituted aromatic	780, 750, 690(W)--No assignment	743(W)--γ(C-H), phenol 711(W)--No assignment 690(W)--γ(C-H), phenol	750(M)--Substituted phenyl 700(W)--Phenyl ring
600-400(W)	--	510(W)--No assignment	460(W)--No assignment	--